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THE PHYSICAL REVIEW

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THE

PHYSICAL REVIEW.

A SPECTRAL LUMINOSITY CURVE EQUATION AND ITS USE.

By E. F. Kingsbury.

SEVERAL attempts have been made to obtain an equation that would express the luminosity curve of the average eye as a function of an equal energy spectrum. Goldhammer,[1] Hertzsprung,[2] and Nutting[3] have each proposed equations that have the general form required. They have all been simple, transcendental equations and have fitted the experimental curves only approximately. The experimental curves have likewise been only approximate and there has been little value in obtaining an equation to fit any one closely.

Recently, however, considerable work[4] has been done which seems to define the luminosity curve rather better than heretofore. While much more work with a still larger number of observers remains to determine it even more accurately, it seemed worth while at this time to get an equation that would fit the latest determination within the limits of these values. Such an equation would be of value in a definition of the luminosity curve and in various computations of radiant efficiency, the mechanical equivalent of light, etc.

In an attempt to obtain an equation the application of a resonance, or absorption equation, at once suggests itself if we desire to solve it from a theoretical viewpoint. At the present time such an equation would necessarily be largely empirical in its details, and an attempt to make it fit the observed points closely would make it too complicated to be useful. The present effort was therefore to obtain by some simple means an arbitrary equation. The equations that have been suggested have

[1] Ann. Ph., XVI., p. 621 (1905).

[2] Z. Wiss. Phot., IV., p. 43 (1906).

[3] "The Luminous Equivalent of Radiation," Nutting, Bull. of Bur. of Stds., V., 1908–9, p. 273.

[4] "Physical Photometry with a Thermopile Artificial Eye," Ives & Kingsbury, Phys. Review, VI, 5 (1915), p. 319.

probably included too few constants and where agreement has been obtained between the calculated and the experimental curves, it seems to have been accidental.

For example, the form proposed by Goldhammer,

$$L_\lambda = R^n e^{n(1-R)}, \tag{1}$$

where $R = \lambda_{max}/\lambda$, has two parameters, one of which, λ_{max}, is the value of the argument at which the function is a maximum. This is fixed by experiment. Consequently, the only change that can be made is to vary the remaining parameter, n, which merely narrows or broadens the curve, fitting only part of the observed points.

Nutting[1] found that with $n = 181$, function (1) would fit the luminosity curve he had determined experimentally very well from about $\lambda = .48\mu$ to $\lambda = .65\mu$, using $\lambda_{max} = .555$. This formula below $.48\mu$ gives values too small, and beyond $.65\mu$ too large, with a total area ($\mu \times L_\lambda$) of

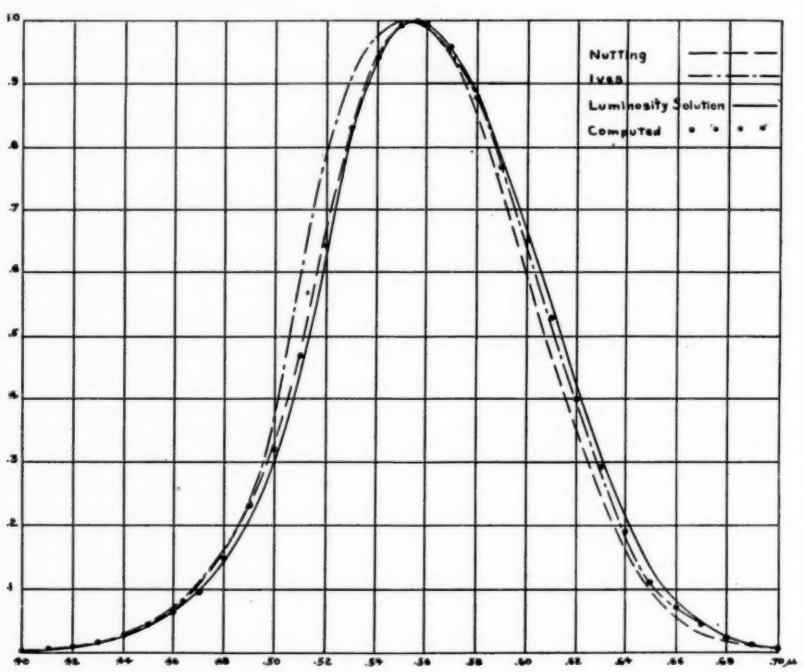


Fig. 1.

Various luminosity curves.

about .103, which is practically the same as the experimental one. The calculated curve evidently adds to the red end what it lacks at the blue end. The accuracy of the luminosity curve at the red end is especially

[1] "The Visibility of Radiation," Nutting, Phil. Mag., 29, p. 301, 1915.

important, because most of our illuminants, at the temperatures we can obtain, have most of the energy on the red side and in multiplying the luminosity curve by the energy curves any errors in the former are magnified considerably.

The method of obtaining the equation given below was as follows:

The exponent, n, of the Goldhammer function (1) was given such a value that it filled the experimental curve throughout a good portion of the blue side and through the maximum, but was low at all other points, *i. e.*, the extreme blue end and all the red side. It was then assumed that the differences between the calculated and the true curves were in each case of the same general form as the one already used. If this were true, then by changing the exponent, n, and the maximum, λ_{max}, and adding a constant coefficient to the whole expression, these new expressions could be added to the first one and their sum should be very close to the true value at all points. Of course chance wholly determined how many terms would be needed. As it happened three in all were sufficient. The equation obtained by the above method was as follows:

$$L_\lambda = .999(R_1 e^{1-R_1})^{200} + .04(R_2 e^{1-R_2})^{400} + .095(R_3 e^{1-R_3})^{1000}, \qquad (2)$$

where

$$R_1 = \frac{.556}{\lambda}, \quad R_2 = \frac{.465}{\lambda}, \quad R_3 = \frac{.610}{\lambda}.$$

The experimental curve taken as the criterion was the one described elsewhere and shown in the solid line in Fig. 1. The heavy dotted line is the curve computed according to equation (2). Fig. 2 shows each of the terms plotted separately and their sum. Where the calculated differs from the other it has been left so purposely as being within the best experimental points. In the future, as the luminosity curve becomes better determined, the calculated curve can be changed easily and more terms added if necessary.

Attention should be called to the fact that function (2) has no relation to the trichromatic theory of color vision and the terms have no connection with the three elementary sensation curves as given by Konig. It is true that if we knew these elemental curves sufficiently well we could obtain three spectral functions corresponding to them whose sum would be equal to the luminosity curve of the eye. This would be very desirable as we could carry the study of the luminosity curve to greater detail.

One of the most important applications of the above function is to compute the luminous power emitted by a black body at various temperatures. If J_λ be the quantity represented by Wien's or Planck's equation, and L_λ the quantity represented by the equation (2), then the

luminous power, expressed in watts per steradian per square centimeter (projected area) of radiating surface can be expressed as follows:

$$\text{Light watts} = \frac{1}{\pi}\int_0^\infty L_\lambda J_\lambda d\lambda = L. \tag{3}$$

The factor, $1/\pi$, enters because it is the normal flux density, σ_0, of radiation per square centimeter per degree[4] we are considering and not the total hemispherical flux, σ, their relation being, $\sigma/\pi = \sigma_0$.

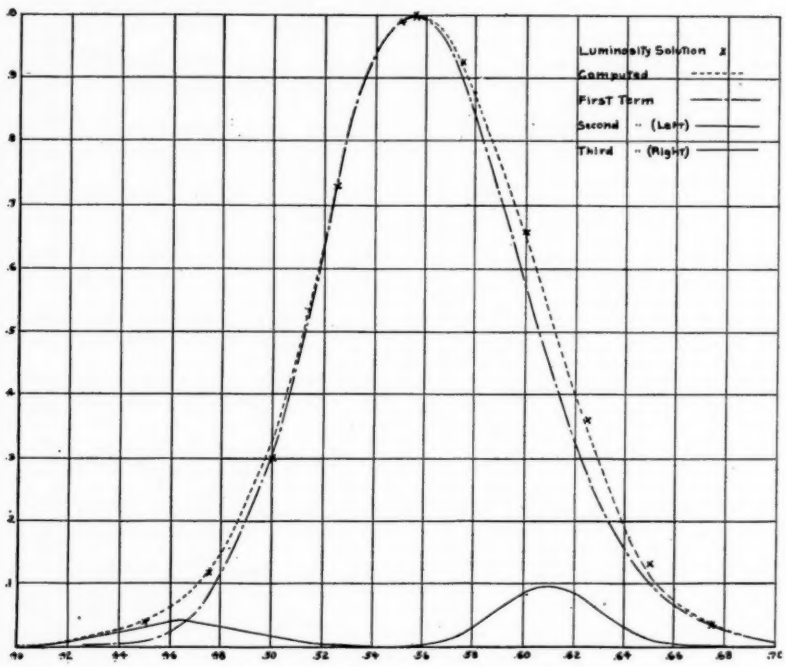


Fig. 2.

Computed luminosity curve showing effect of different terms.

Function (3) has heretofore been evaluated graphically. By means of the new luminosity curve equation it will now be integrated exactly. A formula for the integral will be obtained first by integrating the product of (1), which has the form of each term of (2), by J_λ

$$J_\lambda = c_1\lambda^{-a}(e^{c_2/\lambda k} - 1)^{-1}. \tag{4}$$

Remembering that

$$c_1 = \frac{\sigma c_2{}^{a-1}}{1.0823(a-2)!}$$

we get

$$L = \frac{\sigma}{\pi} A \sum_{\infty}^{m=1} \left(\frac{1}{\frac{mB}{k}+1}\right)^{n+a-1}, \tag{5}$$

where

$$A = \frac{e^n}{1.0823(a-2)!}\left(\frac{c_2}{\lambda_m}\right)^{a-1}\frac{\Gamma(n+a-1)}{n^{n+a-1}}$$

and

$$B = \frac{c_2}{n\lambda_m}.$$

Since $\Gamma(n+a-1) = (n+a-2)!$ and from Stirling's formula[1] for large values of n

$$(n+a-2)! = \frac{\sqrt{2\pi}}{e^{n+a-2}}(n+a-2)^{n+a-3/2}$$

we have

$$A = \frac{\sqrt{2\pi}e^{2-a}}{1.0823(a-2)!}\left(\frac{c_2}{\lambda_m}\right)^{a-1}\frac{(n+a-2)^{n+a-3/2}}{n^{n+a-1}}$$

For Wien's law $a = b$ and $m = 1$ (5) reduces to

$$L = \frac{\sigma}{\pi}\frac{A}{\left(\frac{B}{k}+1\right)^{n+4}}, \tag{6}$$

where

$$B = \frac{c_2}{n\lambda_m}$$

and

$$A = .01922\left(\frac{c_2}{\lambda_m}\right)^4\frac{1}{\sqrt{n}}\left(\frac{n+3}{n}\right)^{n+7/2}.$$

If $c_2 = 14370$ and $\sigma = 5.65 \times 10^{-12}$ watts per sq. cm. per degree[4] and using (2) for L_λ instead of (1), (6) becomes

$$L = \frac{5.65\times 10^4}{\pi}\left[\frac{1.254}{\left(\frac{129.23}{k}+1\right)^{204}} + \frac{.0715}{\left(\frac{77.26}{k}+1\right)^{404}} + \frac{.0359}{\left(\frac{23.56}{k}+1\right)^{1004}}\right]. \tag{7}$$

In Fig. 3 the logarithm of this function is plotted against the logarithm of the absolute temperature, k, and marked A. B is the total energy radiated normally, calculated from the Stefan-Boltzmann law. C is the log of the radiant luminous efficiency, the difference between B and A. The maximum efficiency is about 13.5 per cent. at about 6500° K.

The values used in plotting curves A and D are tabulated in Table 1.

[1] Planck's Heat Radiation, Eng. ed., p. 218.

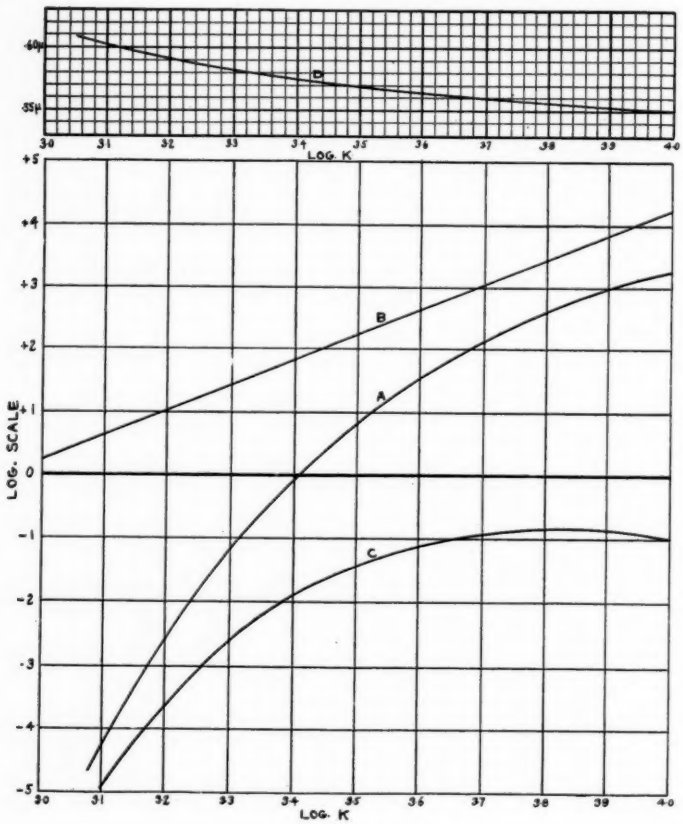


Fig. 3.

A is the log. of the light watts, *L*, computed from equation (7). *B* is the log. of the total energy calculated from the Stefan-Boltzmann law. *C* is the log. of the radiant luminous efficiency = $A - B$. *D* is the Crova wave-length calculated from equation (13). K. = degrees Kelvin.

It is possible to transform these values, which are in terms of light watts per steradian, to candle-power, which is lumens per steradian.

The relation is

$$b_0 = \frac{L}{m}, \tag{8}$$

where m is the constant known as the " mechanical equivalent of light," *i. e.*, the number of watts of luminous flux in the lumen. Conversely, from experimental values for the brightness of the black body the mechanical equivalent of light may be derived.

Experimental values of the candle power per mm.^{2} of a B. B. have been obtained by Lummer and Pringsheim[1] and by Nernst.[2] The values of

[1] Phys. Z., 3, 97 (1901–02).

[2] "The Brightness of a B. B.," Nernst, Physikal. Zeit., Vol. 7, p. 380 (1906).

TABLE I.

K.	L_e	Log K.	Log L_e	Crova Wave-length.	Luminous Efficiency.
1,200	2.173×10^{-5}	3.079	−4.663	.605μ	.00000582
1,400	3.75×10^{-4}	3.146	−3.426	.597	.0000555
1,600	3.25×10^{-3}	3.204	−2.488	.591	.000275
1,800	1.76×10^{-2}	3.255	−1.754	.586	.000933
2,000	6.95×10^{-2}	3.301	−1.158	.582	.00247
2,500	8.30×10^{-1}	3.397	− .081	.576	.0118
3,000	4.45	3.477	+ .648	.570	.0305
4,000	3.66×10	3.602	+1.563	.564	.0794
5,000	1.32×10^{2}	3.700	+2.121	.560	.118
6,000	3.12×10^{2}	3.778	+2.494	.557	.134
7,000	5.78×10^{2}	3.845	+2.762	.555	.134
8,000	9.18×10^{2}	3.903	+2.963	.553	.125
10,000	1.76×10^{3}	4.000	+3.246	.551	.098

the mechanical equivalent obtained by using their figures in (8) scatter widely on both sides of the recent experimental values. They appear also to correspond to a different luminosity scale than that used by us as shown from a consideration of the equivalent or Crova wave-lengths to which these values were supposed to correspond. Fig. 3, curve D, shows the variation of the Crova wave-length with the log. of the temperature for equation (7). This was derived from the following definition.

The Crova wave-length applying to a black body over a small temperature interval is that wave-length whose radiant power varies with any change of temperature by the same fractional part that the total luminous power varies for that temperature change. Thus

$$\frac{\Delta_k J_\lambda}{J_\lambda} = \frac{\Delta_k L}{L}.$$

For the limit, as the increments approach zero, we may write[1]

$$\frac{\partial_k J_\lambda}{J_\lambda} = \frac{\partial_k L}{L}. \qquad (9)^2$$

[1] This definition and equation can be generalized to apply to radiators whose light is varying from other causes than temperature changes. For example, for different Welsbach mantles we can substitute for J_λ, a function of the wave-length and the percentage Ceria. Then we could get a Crova wave-length for mantles of varying composition, which has been done experimentally. (Washington Convention I. E. S., Sept., 1915.)

[2] By the following steps the result obtained by Foote (Journal Wash. Acad. of Sciences, V, 15 (1915), p. 526) can be derived.

Since

$$\partial_k L = \frac{c_2}{\pi k^2}\int_0^\infty \frac{L_\lambda J_\lambda}{\lambda}\, d\lambda dk$$

(10) becomes

$$\lambda_e = \frac{L}{\frac{1}{\pi}\int_0^\infty \frac{L_\lambda J_\lambda}{\lambda}\, d\lambda},$$

which is the same as his equation (5).

Since

$$\partial_k J_\lambda = \frac{c_2 J_\lambda}{\lambda k^2} dk$$

we get

$$\frac{c_2}{\lambda k^2} dk = \frac{\partial_k L}{L}. \tag{10}$$

From (10) we get the relation to the Crova wave-length of the slope of Curve *A* in Fig. 3, thus

$$\frac{\partial_k \log L}{d \log k} = \frac{c_2}{\lambda_c k}. \tag{11}$$

If we differentiate (6) to get $\partial_k L$, we get for the Crova value the simple form

$$\lambda_c = \frac{n\lambda m}{n+4}\left(\frac{B}{k}+1\right). \tag{12}$$

If we take (7) instead of (6) we get

$$\lambda_c = \frac{L}{\frac{\sigma}{\pi}\left[\frac{2.3005}{\left(\frac{129.23}{k}+1\right)^{205}} + \frac{.1553}{\left(\frac{77.26}{k}+1\right)^{405}} + \frac{.0591}{\left(\frac{23.56}{k}+1\right)^{1005}}\right]}. \tag{13}$$

From this equation was calculated the Crova wave-lengths given in the table. Now, Nernst's extrapolation formula

$$k = \frac{11{,}230}{5.367 - \log b_1}$$

calls for a value of λ_c about .56μ and Lummer and Pringsheim's for λ_c about .54, while .58 is called for by the present luminosity curve for the neighborhood of 2000° K. A Crova value of .577μ has been found experimentally for the 1.25 w.p.c. tungsten lamp, which is in excellent agreement with the above luminosity curve.[1]

Detailed discussion of the application of this work to the determination of the mechanical equivalent of light is reserved for a subsequent paper in which will be given new experimental work on the brightness of the black body.

The thanks of the author are due Dr. H. E. Ives for his interest and numerous suggestions in preparing this paper.

THE UNITED GAS IMPROVEMENT COMPANY PHYSICAL LABORATORY,
PHILADELPHIA, PA.,
June, 1915.

[1] The Application of Crova's Method of Colored Light Photometry to Modern Incandescent Illuminants, Ives & Kingsbury, Washington Convention I. E. S., Sept., 1915.

THE HALL EFFECT AND ALLIED PHENOMENA IN TELLURIUM.

BY PETER I. WOLD.

THE following investigation of the galvano- and thermo-magnetic properties of tellurium was prompted originally by a desire to find if any trace of the Hall effect could be detected in a liquid metal.

In view of the fact that the Hall effect has been found in gases[1] and that the theories on this subject give no reason to believe that it should not be found in liquids, experiments have been made at various times attempting to prove or disprove its existence. See for example the work of Everdingen,[2] Roiti,[3] Chiavassa,[4] and Bagard.[5] Tellurium was selected for the study because of its exceedingly large Hall effect at ordinary temperatures.

In the preliminary tests made on tellurium with the above object in view the specimen used showed such unusual and interesting properties that a more thorough investigation of the various galvano- and thermo-magnetic constants seemed justified. This was particularly true in view of the fact that the apparatus necessary for the investigation at the melting point lent itself well to investigation at other temperatures.

APPARATUS.

A Weiss electro-magnet, with pole pieces 10 centimeters in diameter, was used. With these pole pieces a very uniform magnetic field, about 7 centimeters in diameter, could be obtained. This gave a maximum field strength of 10 to 15 thousand gausses per cm.^{2} for the distances between the pole faces which were ordinarily used.

The various effects were all measured by the potentiometer method and the most sensitive galvanometer used had a sensitivity of 130 mm. per microvolt at a scale distance of 4 meters.

Preliminary experiments with the magnet showed that there was considerable residual magnetism on breaking the magnetizing current

[1] Wilson, PHYS. REV., 3, 375, 1914.
[2] Leiden Comm., No. 41, 1898.
[3] Journ. de Phys., 1883.
[4] Ellettricista, 6, 1897.
[5] Journ. de Phys., Ser. 3, T. 5, p. 499, 1896.

and that the amount of residual magnetism depends on the current strength and distance between the poles. It was apparent that for accurate work one could not rely upon a previously plotted curve giving the magnetic field for different values of current. The importance of this will appear later in considering certain parts of the work. Accordingly, arrangements were made to measure the change in the magnetic field, both on making and on breaking the magnetic circuit and at the time of taking observations on the Hall or other effect.

The specimen of tellurium to be studied was fused in a hydrogen atmosphere to prevent oxidation. Generally it was found best to place the tellurium in a test tube of combustion tubing with a small hole blown in the side, about four centimeters from the bottom. Hydrogen was then allowed to flow over the metal and escape through the hole, where it was ignited. The tube was then placed in an electric furnace and the molten metal was quickly poured into a mold, with the hydrogen flowing over it continually.

In its final form the mold consisted of a plate of asbestos slate 4 mm. thick in which a hole 4 cm. by 2 cm. was made. This was closed by cementing to the bottom a thin piece of the same material. The various electrodes, shown in Fig. 1, were embedded in grooves in the plate before the casting was made, being held in place by plaster of paris.

Heating was obtained by means of a double electric furnace. The inner furnace consisted of two brass plates 15 cm. square and spaced 5 mm. apart. Nichrome ribbon was wound around this for a heating coil, being insulated from the brass plates by mica. The second furnace was made of sheets of asbestos board properly spaced to just admit the first furnace and was also wound with nichrome ribbon, the windings being at right angles to those of the first furnace. By this arrangement the temperature gradient through the ends of the furnace was very much reduced and a very uniform temperature was obtained throughout the central portion of the furnace. The furnace, complete and mounted, was about 2 cm. thick. The currents through the two furnace windings were independently controlled.

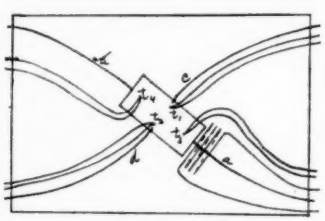


Fig. 1.

In order to obtain the various readings desired four electrodes and four thermo-junctions were connected to the specimen, as shown in Fig. 1. The primary electrodes, *a* and *b*, consisted of platinum ribbon extending across the ends of the specimen, which became fused to the specimen in casting. Copper wires, fused to these platinum strips, served as leads.

The Hall and Nernst effects were measured by means of the electrodes c and d, consisting of copper wires fused to short pieces of platinum. Copper cannot be used directly in contact with tellurium for it dissolves readily in molten tellurium.

As near to the last two electrodes as possible were placed two copper constantan junctions, t_1 and t_2. For reasons which will appear later, these two junctions were insulated from but embedded in the tellurium. The insulation consisted of a glass sheath about 1/20 mm. thick. Arranged longitudinally in the specimen were two platinum-platinum rhodium junctions, t_3 and t_4. These junctions were fused into the tellurium, being in metallic contact therewith.

The temperature gradient required in the specimen for the thermomagnetic effects was obtained by a small heating coil of 8 turns threaded through holes in the base plate near one end of the specimen, as shown in Fig. 1. By suitable control of the current in this coil any reasonable temperature gradient could be obtained.

HALL EFFECT.

The preliminary observations were made on a specimen of tellurium, obtained from Baker and Co., of fair degree of purity. The specimen was 2 cm. square. It was repeatedly heated to a molten condition and search made for the Hall effect. With the galvanometer then in use no definite results were obtained. Certain deflections were noted but they were irregular and may well have been due to mechanical motion of the liquid metal. Readings were taken at various temperatures during the heating and the results consistently showed a change from a positive to a negative Hall effect at a temperature in the neighborhood of 125° C. followed by a reversal to a positive value in the neighborhood of 225°. These results were so surprising that it seemed well to subject them to more careful examination. It was thought that the effect might be due to impurities and consequently work was started to secure especially pure tellurium. This part of the work was done by Mr. D. T. Wilber, of Cornell University. A new supply of tellurium was obtained from Eimer and Amend and subjected to the following treatment:

$$Te + 4HNO_3 = TeO_2 + 4NO_2.2H_2O,$$

$$3TeO_2 + 2CrO_3 + 6HNO_3 = 3TeO_3 + 2Cr(NO_3)_3 + 3H_2O.$$

This was evaporated with an excess of HNO_3 until the telluric acid, $H_2TeO_4.2H_2O$ or $TeO_3.3H_2O$, separated out. This was recrystallized six times by dissolving in hot water, then adding nitric acid and cooling. It was washed once with alcohol to remove traces of $Cr(NO_3)_3$.

The pure acid was reduced to the metal by boiling with recrystallized hydrazine hydrochloride:

$$2TeO_3 + 3N_2H_4.2HCl = 2Te + 6HCl + 3N_2 = 6H_2O.$$

The finely divided metal was washed with water to free it from hydrochloric acid, hydrazine or telluric acid.

The metal was then reduced to the massive form by melting in a section of combustion tubing, there being a continuous stream of hydrogen passing over and through the mass. This product was treated in the manner described on page 3 in order to get it in the desired form.

Measurements were made to find the relation between the Hall effect and the magnetic field at constant temperature. The results obtained, by taking a number of runs at different temperatures, are given in Table I., in which

H = strength of field in gausses per cm.^{2}

E_a = Hall effect in microvolts with the magnetic field in one direction.

E_b = Hall effect with field in other direction.

E = mean of these two.

R = Hall constant.

$D = E_a - E_b$.

R is obtained from the usual expression for the relation between the various quantities involved; viz.,

$$R = \frac{E}{Hib},$$

where i is the current density and b is the distance between the Hall electrodes.

Fig. 2 shows graphically the relation between the Hall effect, repre-

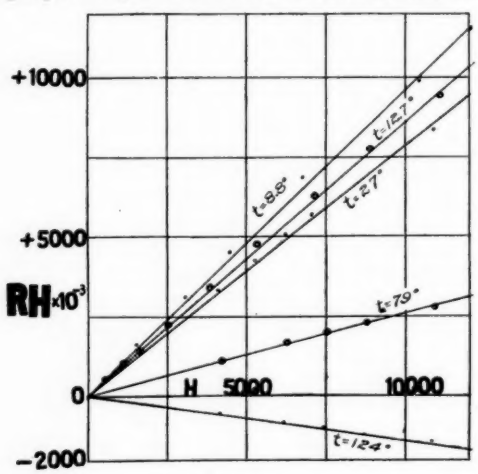


Fig. 2.

Hall Effect and Magnetic Field.

TABLE I.

Hall Effect.

t = 12.7° C. Current = .234 amp.

H	E_a	E_b	E	$RH \times 10^{-3}$	R	D	$D/H^2 \times 10^{+7}$
586	+259	+263	+261	+516	+881	− 4	
1,151	524	506	515	1,015	881	+18	
1,684	726	724	725	1,413	839	2	7
2,595	1,154	1,139	1,147	2,222	857	15	22
3,884	1,747	1,722	1,735	3,375	868	25	17
5,365	2,460	2,415	2,438	4,740	884	45	16
7,193	3,301	3,204	3,253	6,250	869	97	19
8,930	4,043	3,870	3,957	7,710	864	173	22
11,134	4,936	4,692	4,814	9,390	844	244	20
			t = 27.1° C.	Current = .236 amp.			
577	+229	+228.5	+229	+446	+773	+ 0.5	15
1,660	674	655	665	1,289	776	19	69
3,060	1,235	1,220	1,228	2,360	771	15	16
4,160	1,724	1,697	1,711	3,300	793	27	16
5,320	2,217	2,166	2,192	4,240	798	51	18
6,280	2,648	2,564	2,606	5,050	804	84	21
7,080	2,975	2,864	2,920	5,650	798	111	22
8,820	3,636	3,474	3,555	6,890	781	162	21
10,950	4,432	4,174	4,303	8,350	763	258	22
			t = 79.0° C.	Current = .234 amp.			
2,160	+290	+276	+283	+535	+248	+14	30
4,265	580	539	560	1,080	254	41	23
6,310	865	789	827	1,650	262	76	19
7,580	1,069	952	1,011	1,970	260	117	20
8,790	1,207	1,039	1,123	2,260	257	168	22
10,900	1,511	1,299	1,405	2,755	253	212	18

sented by RH, and the magnetic field. The curves are straight lines, the slope of each being the sum of the ordinates divided by the sum of the abscissæ for the points shown for that curve. It will be noted that in each case the points for intermediate values of field lie above the line, this departure from the straight line relation can also be noted by observing the values for R in Table I. In each case, even where the effect is reversed, the intermediate values for R have a higher value, considered positively. The discrepancy appearing in the first two lines of the first set is probably due to the greater relative error in taking observations in weak fields.

A certain amount of dissymetry was observed in the Hall effect as obtained for fields of different directions. This is shown under the column headed D and will be discussed later in connection with the change of resistance.

ETTINGHAUSEN EFFECT.

The Ettinghausen effect, or the transverse galvanomagnetic temperature difference, was measured by means of the copper constantan thermojunctions, t_1 and t_2 of Fig. 1. By connecting these two junctions in opposition it was possible to increase the accuracy of the work greatly. To do this, however, it was necessary that the junctions should be insulated from each other. This was done in the manner described elsewhere. The arrangement was such that a scale deflection of 1 mm. was equivalent to .0002°. As a rule measurements on the Ettinghausen effect were taken along with those on the Hall effect. Upon application of the field the reading for the Hall effect was taken quickly—a few seconds being sufficient—and then the attention was turned to the Ettinghausen effect. This effect was given at least a minute in which

TABLE II.

Ettinghausen Effect.

H	Δt	$P \times 10^5$
1,668	.006	+ 8.06
3,316	.009	6.05
6,330	.014	4.93
9,632	.029	6.71
11,750	.033	6.27
13,450	.035	5.81
15,190	.041	6.03
15,640	.043	6.14
	$t = 8.8°$.	
1,577	.0058	+ 7.12
3,110	.0116	7.20
4,520	.018	7.55
6,807	.025	7.05
10,482	.038	6.88
12,625	.046	7.03
15,390	.060	7.47
	$t = 27.1°$.	
577	.0035	+11.8
1,660	.011	12.7
3,060	.020	12.7
4,160	.024	11.2
5,320	.029	10.6
6,280	.035	10.9
7,080	.039	10.7
8,820	.042	9.3
10,950	.059	10.5

to build up. Considerable difficulty was found in deciding when the deflection had reached its maximum. This was due to a drift caused by slow temperature changes in the specimen, which might be in one direction or the other. In finding the Ettinghausen effect under any conditions temperature readings were taken in the order and with the magnetic quality of 0, +, 0, −, 0. This gave four temperature changes. With the primary current reversed a similar set of four temperature changes was obtained. The mean of these eight readings is given in the table as a value for Δt under the given conditions.

The values obtained in a number of different runs, showing the relation between this effect and the magnetic field, is given in Table II.

In this table Δt is the transverse temperature difference set up or caused by the magnetic field. P is the Ettinghausen constant as defined in the usual manner by the equation

$$P = \frac{\Delta t}{Hib},$$

in which i is the current density and b the distance between the junctions. The results are shown graphically in Fig. 3, in which Δt is used for ordinates and field strength for abscissæ. Considering the relatively large errors which enter into the measurement of such small temperature changes under such conditions the results seem to justify the conclusion that the Ettinghausen effect in tellurium is proportional to the magnetic field.

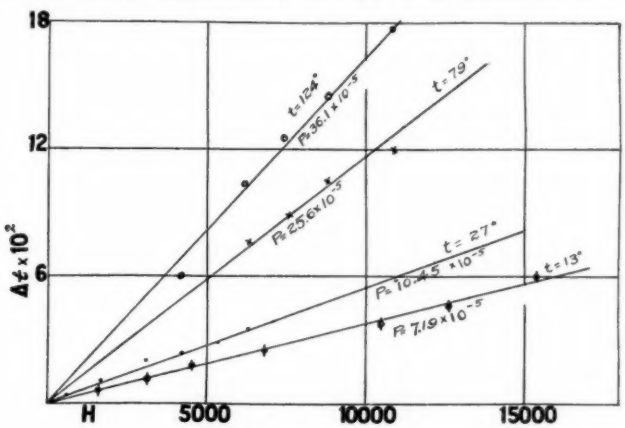


Fig. 3.

Ettinghausen Effect and Magnetic Field.

The value for P found for tellurium by Ettinghausen is $+ 20 \times 10^{-5}$. Lloyd[1] gives $P = 14 \times 10^{-5}$ to 29×10^{-5} at 65° and for $H = 5500$.

[1] Amer. Journal of Science, 12, p. 57, 1907.

LONGITUDINAL EFFECT.

A third electromagnetic effect is that commonly known as the longitudinal effect, and which is commonly expressed as change in resistance. By means of the platinum wires of the junctions t_3 and t_4 the potential between two points in the specimen, arranged longitudinally, could be found. In series with the specimen was a standard resistance. Connections were made from this to a potentiometer connected to a very sensitive galvanometer and currents could then be measured accurately to one part in 20,000. Two potentiometers were adjusted simultaneously and, in spite of variations in the battery current, instantaneous values of the current and of the potential difference between the two points in the specimen were obtained. Upon application of the magnetic field there was a change in the potential difference in the specimen indicating a change in resistance. The results obtained in two runs are given in Table III., in which H is the field strength, W_0 is the resistance

TABLE III.

Resistance.

H	W_0	$w'/W_0\times10^5$	$w''/W_0\times10^5$	$w/W_0\times10^5$	$w/W_0H^2\times10^{13}$	$D\times10^5$	$D/RH\times10^{12}$
1,588	.56335	+ 74.6	− 40.0	+ 17.3	+687	115	751
3,085	313	+ 194.8	− 26.6	+ 84.1	+890	221	748
4,430	666	+ 317	− 2.6	+ 157.2	+801	320	750
6,730	429	+ 636	+ 129.4	+ 383	+847	507	782
10,352	231	+1208	+ 439	+ 824	+768	769	770
12,515	222	+1548	+ 646	+1097	+700	902	749
15,300	222	+2092	+1028	+1560	+666	1064	722
1,690	.58918	+ 56.8	− 28.0	+ 14.4	+505	85	642
3,120	916	+ 155	− 27.0	+ 64.0	+657	182	744
4,340	913	+ 239	− 4.9	+ 117	+624	244	717
5,660	892	+ 372	+ 48.3	+ 210	+655	324	732
6,340	895	+ 455	+ 90.7	+ 273	+679	364	732
7,130	735	+ 560	+ 162	+ 361	+710	398	713
8,840	752	+ 755	+ 251	+ 503	+645	504	728
10,960	758	+1049	+ 438	+ 744	+620	611	725

in zero magnetic field during the observations at the value of field indicated, w' is the change in resistance with the magnetic field in one direction, w'' is the change with the field in the opposite direction, and w is the mean of these. D is the difference between w' and w''. The positive value of w/W_0 indicates an increase of resistance.

The change in the value of W_0 during the course of a run is due to slight temperature drift. It will be shown later that the resistance of tellurium is very senstitive to temperature changes.

In view of the fact that this longitudinal effect does not change direction with the change in direction of the magnetic field it has been assumed that the effect should be proportional to the square of the magnetic field. This law is fairly well obeyed in some substances. In case of bismuth, which has been studied the most carefully in this respect, it appears that the law holds for weak fields, but for stronger fields the effect is nearly proportional to the first power of the magnetic field. Column six in the table shows how this law holds in this case. The variations between the different values of w/W_0H^2 seem to be entirely irregular and are probably due to experimental errors.

Referring to Table I. it is to be noticed that there is a dissymmetry in the value of the Hall effect, depending on the direction of the magnetic field. In his work on bismuth Van Everdingen[1] has shown that this dissymmetry can be explained by means of the change in resistance. If the Hall terminals are not on an equipotential line, but are slightly displaced, a component of the total potential drop through the specimen, due to the primary current, will show itself at the Hall terminals and, of course, will not reverse with the magnetic field. Upon the application of the magnetic field the Hall effect will be superimposed upon this potential difference, in the one case adding to it and in the other case subtracting from it. The Hall effect is obtained by taking the difference between the potentiometer reading for zero field and for field H. If the component of the potential at the Hall terminals remains constant there will be no error from this source. If, however, the current remains constant and the resistance changes on the application of the field it is obvious that the component potential across the Hall terminals will change in the same proportion. Consequently the value of the Hall effect obtained by taking the difference between the potentiometer readings with and without the field will be in error. If the change in resistance reversed with the magnetic field it would be impossible to separate it from the Hall effect and so find the true value of the Hall effect. Since it does not reverse it is apparent that in the one case it will increase the value of the Hall effect and in the other case decrease it so that a correct value for the Hall effect is obtained by taking the mean of the two values so obtained. This method has been followed out as shown in Table I., in which E_a gives the Hall effect obtained with the field in one direction and E_b that obtained with the field in the opposite direction. The correct value of the Hall effect is the mean of these two, given under E.

If this dissymmetry is due to the change in resistance it should follow

[1] Leiden Communication, No. 26, 1896.

the same law. Assuming, from the results in Table III., that the change in resistance is proportional to H^2 then there should be a linear relation between D and H^2, or D/H^2 should be a constant. Column 8 of Table I. shows the values obtained for D/H^2. Excluding the values for very weak fields, in which the dissymmetry is very small and subject to relatively large errors, it will be noticed that the agreement among the values of D/H^2 is very satisfactory, thus giving a verification of Van Everdingen's theory.

A dissymmetry in the change of resistance was also found, the value being always larger with the magnetic field in one direction than in the other. It even occurred that in weak fields there was an apparent decrease in resistance with the field in one direction. Columns 3 and 4 of Table III. show this. The mean of the two values was, however, positive in all cases. It occurred to the author that a similar line of reasoning may be used to explain this dissymmetry as was used in the case of the Hall effect. If the two leads, by means of which the potential drop along the specimen is measured, are not exactly on a line of current flow it will occur that, upon the application of the magnetic field, a component of the Hall effect will be found across these potential leads. Since the resistance change does not reverse with the magnetic field and since the Hall effect does reverse, in the one case the resistance will be increased by the component of the Hall effect and in the other case will be decreased. Consequently the correct value of the resistance change will be obtained by taking the mean of the two values so obtained. Since the Hall effect is very large in tellurium it is not surprising that the small component of it which comes across the potential leads should more than overbalance the resistance increase, giving an apparent decrease in resistance. Since the resistance increases as the square of the magnetic field while the Hall effect increases with the first power only the increase in resistance finally outstrips the Hall effect. If this dissymmetry is due to the Hall effect it should be proportional to it and consequently there should be a linear relation between D and RH, or D/RH should be a constant. In column 8 of Table III. will be found the values of D/RH. The agreement is very satisfactory indeed.

One other galvanomagnetic effect, *i. e.*, the longitudinal change in temperature, was sought for but, if present, was masked by a component of the Hall effect. If the junctions t_3 and t_4 had been insulated from the specimen, as were t_1 and t_2, it might have been possible to find it.

THERMOMAGNETIC EFFECTS.

In order to study the thermomagnetic effects a small heating coil near one end of the specimen was arranged as described on page 3. Since there

was no corresponding cooling agent at the other end the average temperature of the specimen was raised and thus the study at the lower temperatures was limited. The temperature gradient was measured by means of junctions t_3 and t_4, which are spaced 2.6 cm. apart and approximately equidistant from the center.

NERNST EFFECT.

The relation between the Nernst effect and the magnetic field is shown in Table IV. The average temperature is given by t and the temperature gradient by dt/dl. The second column gives the Nernst effect in absolute

TABLE IV.

Nernst Effect.

H	$QH \times 10^{-2}$	Q
$t = 45.8°$ C., $dt/dl = 21.4/2.6 = 8.23$.		
2,230	6.3	.283
4,340	12.5	.287
6,520	18.8	.288
7,890	22.3	.283
9,080	25.3	.279
11,250	29.7	.264
$t = 204°$ C., $dt/dl = 17.8/2.6 = 6.85$.		
2,180	5.8	.264
4,330	11.6	.268
6,500	17.7	.273
7,870	20.9	.266
9,120	23.7	.260
11,210	28.4	.253
$t = 43.1°$ C., $dt/dl = 19.6/2.6 = 7.54$.		
2,160	11.1	.512
4,270	22.1	.517
6,400	33.5	.523
7,830	40.8	.522
9,030	46.4	.514
11,200	55.2	.492

units for a plate of unit dimensions in which there is unit temperature gradient. The third column gives the constant for the Nernst effect, where Q has the usual significance expressed by the relation

$$Q = \frac{E}{H \frac{dt}{dl} b}.$$

Lloyd[1] gives $Q = .36$ at 33°.

[1] Amer. Journ. of Sci., 12, p. 57, 1907.

The relation between QH and H is also shown graphically in Fig. 4. The slopes of the straight lines shown are equal to the sum of all the ordinates of the points shown divided by the sum of all the abscissæ. It will be noted that there is a slight departure from the straight line relationship, there being a slight curvature upwards. This same is

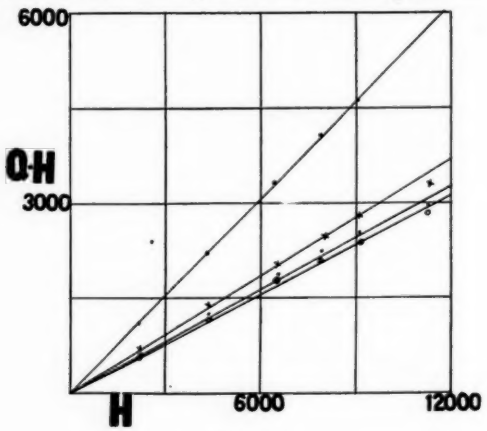


Fig. 4.
Nernst Effect and Magnetic Field.

apparent from a perusal of the values of Q in Table IV., the values of Q increasing slightly with increase of field and then decreasing. The same effect was noted in the case of the Hall effect.

LEDUC EFFECT.

The relation between the Leduc effect and the magnetic field is shown in Table V. The manner of taking observations was the same as that given for the Ettinghausen effect, the same order of magnetic changes being followed and being repeated. Each value of Δt is therefore the mean of eight readings.

TABLE V.

Leduc Effect.

$t = 114°.$, $dt/dl = 30°/2.6 = 11.5°$, $Q = 1.07$.

H	Δt	$SH \times 10^{+3}$	$S \times 10^{+6}$
3,120	.412'	20.4	6.5
6,390	.729	36.1	5.7
7,750	.973	48.1	6.2
8,920	1.162	57.5	6.5
10,700	1.243	61.6	5.8

The Leduc constant is obtained from the usual equation

$$S = \frac{\Delta t}{H \frac{dt}{dl} b}.$$

The values for S show a good agreement considering the great difficulties in the measurement of such small temperature differences. The conclusion is justified that the Leduc effect is proportional to the magnetic field.

Lloyd[1] found $S = +4 \times 10^{-6}$ for tellurium at 34°.

An unusually large value for the Nernst effect was obtained at this time, being given by $Q = 1.07$.

RELATIONSHIP BETWEEN THE VARIOUS EFFECTS AND TEMPERATURE.

The dependence of these various effects upon temperature has been studied up to the melting point of tellurium and will be discussed in the same order as for the dependence upon the magnetic field.

HALL EFFECT AND TEMPERATURE.

In their original investigations on tellurium Ettinghausen and Nernst[2] stated that the Hall effect decreases with an increase of temperature. Smith[3] has also recently investigated the effect of temperature up to 370° C. Smith finds a rapid drop as the temperature rises until 180° C. is reached. Between 180° and 275° the effect decreases slowly. At 275° Smith notes a sudden rise of about 100 per cent. after which there is again a gradual drop. Smith connects this discontinuity with the fact that there are probably two crystalline forms present in tellurium, this fact being pointed out by Haken[4] as a result of work done on the resistance and the thermo-electric power of tellurium.

In the preliminary work, mentioned previously, the author was surprised to find that the Hall effect started with a positive value and diminished rapidly with rise of temperature, changing into a negative value and later, with further rise in temperature, reversing to a positive value again. The same results were obtained repeatedly. The fact that a reversal in the Hall effect in tellurium had never been noted led to the suspicion that it was due, in this case, to some impurity in the specimen used. At the same time further investigation of this unusual phenomenon seemed justified. Accordingly tellurium, purified in the manner previously indicated, was subjected to careful study. The results of the preliminary trial were fully verified, as shown in Fig. 5, in which the ordinates represent Hall effect for a constant magnetic field of 7,580 C.G.S. units, and a constant current of .2425 ampere. The initial value of the Hall effect differs radically in different successive runs but in every case there is a

[1] Amer. Journ. of Sci., 12, p. 57, 1907.
[2] Acad. Wiss., Wien, Anz., p. 173, 1886.
[3] PHYS. REV., 5, p. 351, 1913.
[4] Ann. d. Phys., 32, p. 291, 1910.

definite double reversal in the sign of the Hall effect. The initial value depends, apparently, upon the heat treatment. The runs were taken in the order in which the curves are numbered. The runs 1, 2 and 3 followed each other on successive days and it appeared as though the extent to which the specimen became negative was decreasing and that

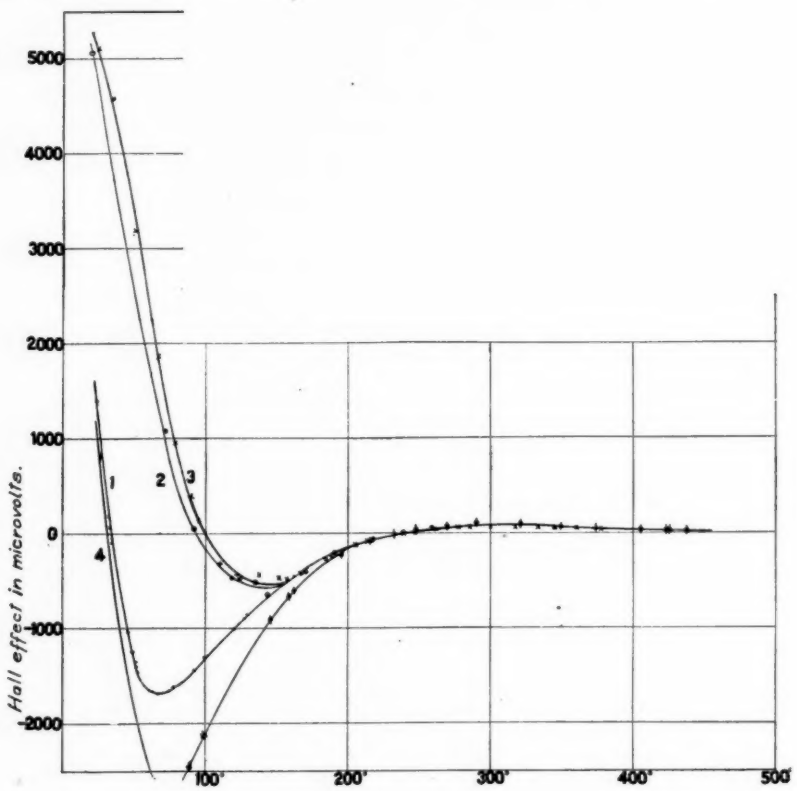


Fig. 5.

Relation between Hall Effect and Temperature.

finally the change would not appear. After this, various other properties were studied and the specimen was subjected to a varied heat treatment. Another run was then made on the Hall effect resulting in Curve 4 which shows an enormous negative value. Not expecting such results large temperature steps were taken and consequently the turning point of the curve was entirely missed. One can therefore only estimate the magnitude of the negative Hall effect attained in this run. It is of importance to note that, while there is a great difference in the curves at lower temperatures, the curves gradually approach each other and cross to a

positive value at the same temperature, viz., 245° C. From there on the curves agree within the errors of observation.[1]

According to Haken and others tellurium occurs in two crystalline modifications. The α modification is stable below 354° C. and the β modification is stable above this temperature. As tellurium is cooled from this temperature the β form goes over into the α form, but the process is rather slow and, in general, some of the β form will not have time to pass over before it is cooled to such an extent that it cannot make the transition. At ordinary temperatures, then, both forms are present and the relative amounts will depend on the previous heat treatment.

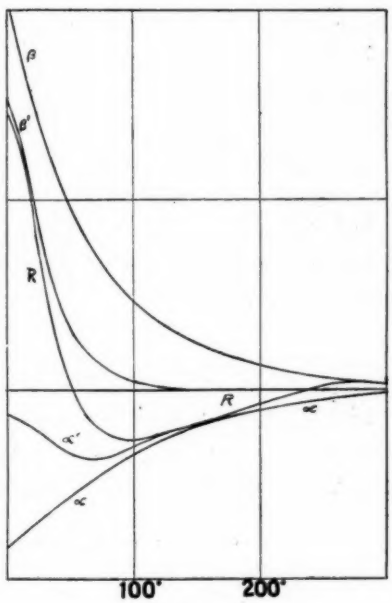


Fig. 6.

Relation between Hall Effect and Temperature.

The peculiar effects here obtained may be tentatively explained on the basis that the β modification has a positive and the α modification a negative Hall effect. Referring to Fig. 6 we may assume, for the present, that the Hall effect for pure β tellurium would be given by the curve β and that for pure α tellurium by the curve α. At room temperature there may be a large proportion of the β tellurium, but with rise in temperature the mobility of the molecules increases and they go over in the α form. Assuming the mass law to hold in this case and bearing in mind the continually decreasing amount of this form, the actual Hall effect contributed by the β tellurium would be given by curve β'. Similarly, in view of the relatively small initial but continually increasing

[1] Since writing the above a chemical analysis of the tellurium used in this work has been made by Prof. R. P. Anderson, of Cornell University. In spite of the superiority of the method used and the great care exercised in the preparation of the tellurium it seemed possible that the unusual results obtained were due to the presence of some impurities, in particular tellurium dioxide. The analysis showed that, aside from tellurium dioxide, the impurities were too small to be detected. The powdered tellurium contained about 17 per cent. of the dioxide. The average of two tests on the fused metal gave a tellurium content of 100.5 per cent. The analyst states that this high result is, without doubt, due to a slight oxidation of the tellurium during the drying operation at the close of the analysis. The error is in the direction to indicate high purity and in any event the amount of oxide present in the fused metal is exceedingly small and is certainly no larger than in that used by previous experimenters.

amount of α tellurium, the actual Hall effect due to it would be given by curve α'. The sum of these two curves, *i. e.*, curve R, would give the resultant Hall effect, which shows a reversal to the negative sign at a temperature depending on the heat treatment.

At a higher temperature the β tellurium becomes stable and consequently the α reverts into the β form, with its positive Hall effect. As a result we find the curve R crossing the axis to a positive value. Having reached a maximum when all the α has been transformed in β tellurium, it follows the regular law of decrease for the β tellurium.

In Fig. 6 no attempt has been made to give the curves quantitative values. The figure is qualitative only.

The above hypothesis can probably be tried out by giving the specimen a systematic and varied heat treatment, and it is hoped that a thorough investigation along this line can soon be made.

It is to be noted that the actual temperatures of reversal are materially below the temperature of 354° C., given by Haken as the transition temperature.

ETTINGHAUSEN EFFECT AND TEMPERATURE.

Simultaneously with the readings on the Hall effect, resulting in the curves just discussed, readings were taken on the Ettinghausen effect. The values obtained for the constant P are plotted in Fig. 7. Curve 1

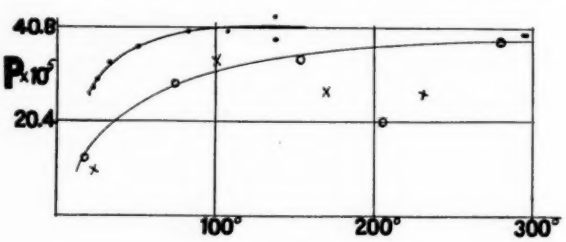


Fig. 7.

Relation between Ettinghausen Effect and Temperature.

corresponds to Curve 1 of Fig. 5. The points obtained during the runs corresponding to Curves 2 and 3 are shown, respectively, by circles and by crosses. While the values do not agree with those of Curve 1 they show in all cases a decided increase in the value of the effect as the temperature increases. Both of the last two runs show a big drop in value in the neighborhood of 200° C. and then an increase. In view of the difficulties in taking these readings there is some doubt as to whether this drop is a real effect or is due to experimental errors.

RESISTANCE AND LONGITUDINAL EFFECT WITH TEMPERATURE.

While readings were being taken on the Hall effect and the Ettinghausen effect readings were also taken on the resistance and the change of resistance in the magnetic field. The method used has been described.

Fig. 8 shows the relation between specific resistance and temperature.

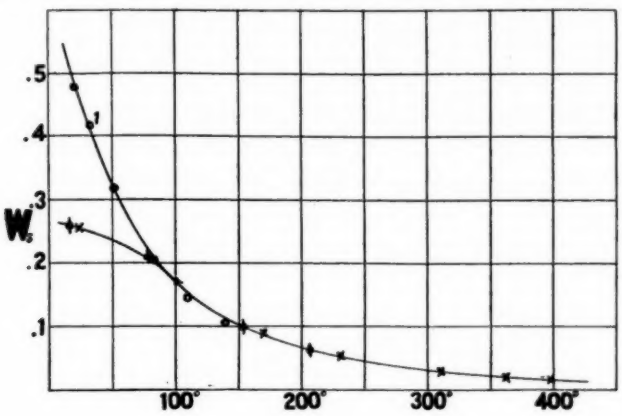


Fig. 8.

Relation between Resistance and Temperature.

The ordinates are expressed in ohms per cm.[3] Curve 1 corresponds to Curve 1 of Fig. 5. It will be seen that the resistance at room temperature depends on the heat treatment and that in the neighborhood of 150° C. the curves come together after which they repeat consistently. The results obtained from the runs 2 and 3 agree throughout. The specific resistance at room temperatures is enormous, being about 500,000 times that of copper.

Tellurium has been classed by Koenigsberger[1] with certain other materials as a conductor of the second class. Its decrease of resistance with increase of temperature has been explained as due to the fact that the number of free electrons, which are effective in producing metallic conduction, is not constant, as is assumed in ordinary metals, but increases with increase of temperature. In ordinary metallic conduction the increase of resistance with temperature is due to the increased collision activity of the electrons. This factor is also effective in conductors of the second class but is masked by the great increase in the number of free electrons. According to Koenigsberger a temperature is reached at which the further increase of electrons is much decreased or ceases entirely. From this point on these conductors should show an increase of resistance with rise in temperature. No such effect can be detected in the resistance

[1] Ann. d. Phys., 32, p. 179, 1910.

curve of tellurium up to a temperature of 400° C., and there seems to be no indication of its appearance before the liquefaction temperature of about 450° C. is reached.

The dependence of the magnetic change of resistance on the temperature is shown in Fig. 9, in which the ordinates give $\Delta w/W$, *i. e.*, the ratio of the increase of resistance in the magnetic field to the resistance in zero field. The constant field strength used was 7,580 gausses and the current was .2425 ampere. As in the case of the resistance curves, the results repeat above about 150° C. Curve 1 corresponds to Curves 1 of Figs. 5 and 8. The largest relative increase occurs when the resistance is largest.

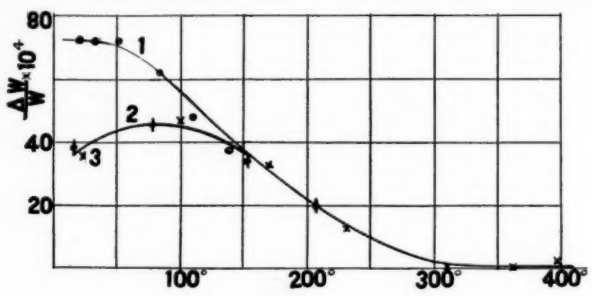


Fig. 9.

Relation between Longitudinal Effect and Temperature.

NERNST EFFECT AND TEMPERATURE.

With increase of temperature the Nernst effect is found to increase quite rapidly to a maximum and then decrease continually to the liquefaction temperature. This is shown in Fig. 11.

THERMO-ELECTRIC POWER AND TEMPERATURE.

Measurements were made on the thermo-electric power of tellurium, use being made of the platinum terminals of the thermo-junctions 3 and 4. In view of the very large thermo-electric power measurements could be made with small temperature difference between the two junctions, ranging from 2 to 10 degrees. The small temperature gradient still permitted measurements of the Nernst effect. In view of the comparative smallness of the Nernst effect, the Hall effect could also be obtained by first measuring the Nernst effect and then sending a primary current through the specimen. The potential difference last found would give the sum of the Nernst and Hall effect. Knowing the former the Hall effect could then be obtained. Thus it was possible to obtain, simultaneously, values of the Hall and the Nernst effects and of the thermo-electric power. The results are shown in Fig. 10 and Fig. 11. Curves

1 and 2 of Fig. 10 and Curve 3 of Fig. 11 show, respectively, the Hall effect, the thermo-electric power and the Nernst effect. Curves 1′, 2′ and 3′ are the corresponding curves for a similar run. There seems to be no particular relationship between the curve for the Nernst effect

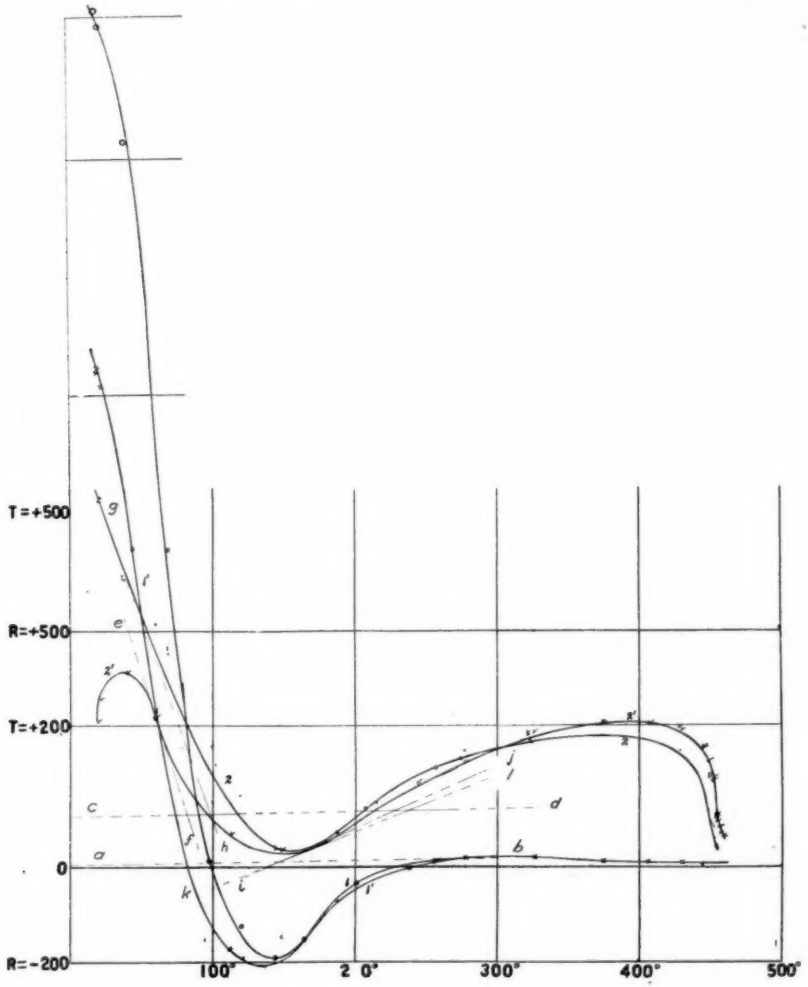


Fig. 10.

Comparison of Hall Effect and Thermo-electric Power at Different Temperatures.

and the other two curves, but the relationship between the Hall effect and the thermo-electric power is most striking.

It has been remarked by a number of investigators that, in general, a high thermo-electric power is accompanied by a high Hall effect. Wick[1]

[1] PHYS. REV., 27, p. 76, 1908.

has arranged a large number of substances according to their thermo-electric powers and finds that, with few exceptions, the Hall effect follows the same order, both in magnitude and in sign.

In this work, however, we have an unusual and remarkable curve for the Hall effect accompanied by an unusual and remarkable curve for thermo-electric power (which is ordinarily an approximately straight line) and following it so closely in form that the two curves might well be mistaken for each other. The author is not aware of any case in which such an intimate relationship between Hall effect and thermo-electric power has been shown. One is almost compelled to believe that the thermo-electric power should reverse with the Hall effect. On one or two occasions, earlier in the work, a reversal in the thermal E.M.F.

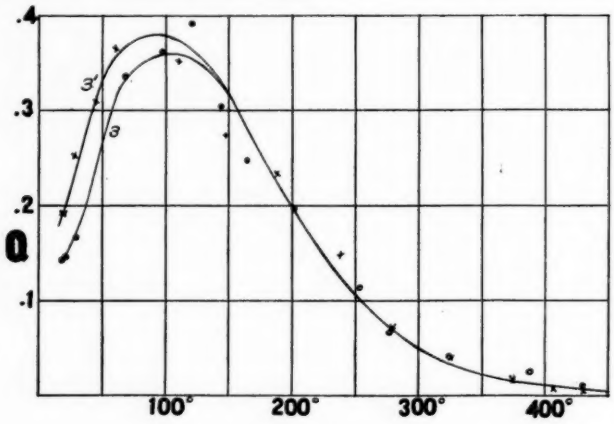


Fig. 11.

Relation between Nernst Effect and Temperature.

was found, but at that time was laid down to error in observation. During the more careful test this reversal has not occurred, but the form of the two curves together suggest that this might well be expected and is a matter depending on the heat treatment.

The thermo-electric power is here given with respect to platinum. The lead line, $a - b$, is shown slightly above it. The lead line has been taken as the standard in thermo-electric measurements because of the fact that its Thomson effect is very nearly zero. The slope of the thermo-electric power line, with respect to lead, gives the Thomson effect for any given material. So far as the Thomson effect is concerned we might equally well take any line parallel to the lead line as our standard and lead has been chosen because it is that metal which has the smallest Thomson effect, as a result of which its thermo-electric power line is practically horizontal. It is apparent then that lead is not a fundamental

standard but one of convenience. A line, *c–d*, has been drawn parallel to the lead line and, for the present, will be considered as the base line for thermo-electric power. If tellurium occurs in two crystalline forms, with a relatively large proportion of β tellurium "caught" at room temperature, as previously suggested, the first part of the curves shown will apply closely to the properties of the β modification. A gradual transition commences as soon as the temperature rises. The tangent to the Curve 2 in its early stages, shown by the dotted ling *g–h*, represents the thermo-electric power for the relatively pure β modification. The point where this line intersects our new base line indicates the temperature at which the thermo-electric power reverses with respect to this base line. It will be noted that this is the same temperature—about 99° C. —as that at which the corresponding Hall effect reverses, as seen by Curve 1.

The line *e–f* similarly represents the thermoelectric power in the early stages of Curve 2′. This line intersects the new base line at the temperature 83° C., which is the same temperature as that at which the corresponding Hall effect reverses in sign, as shown by Curve 1′.

Going to the other side of the minimum points of these curves, we must conclude that the transformation into the α modification is complete when a temperature of about 185° C. has been reached. The lines *i–j* and *k–l* seem to fairly represent the slopes of the thermo-electric power curves for this temperature region, and therefore are the thermo-electric power curves for the pure α modification. The temperatures at which these lines *i–j* and *k–l* intersect the base line *c–d* are the same as those at which the corresponding Hall effects reverse from the negative to the positive signs.

It is apparent that there is a reasonable amount of freedom in choosing the location of the line *c–d* as well as the tangents *e–f* and *g–h*, at the same time there was no difficulty in bringing about the remarkable agreement between the points of intersection noted above and it is an interesting possibility that we may here have the basis for the location of a more fundamental line than the lead line from which to measure thermo-electric forces. The author has, however, no theoretical considerations to support the experimental evidence.

The change in slope of the thermo-electric power lines beyond 250° C. is to be noted. Here we are having the change from the α into the β tellurium. There is probably a large time lag in this transformation, and therefore the slope of the pure β tellurium is not reached till we are near the melting point.

LEDUC AND LONGITUDINAL THERMOMAGNETIC EFFECTS.

It was expected that the relation between temperature and the Leduc effect would be found. Unfortunately one of the transverse thermo-junctions was broken during one of the heat runs and consequently no readings have been taken.

Attempts were also made to find the effect of the magnetic field upon the thermo-electric power as well as upon the longitudinal temperature gradient. There was clear evidence of the latter at least, but the results have been so inconsistent and irregular that they are not given.

HALL EFFECT IN LIQUID TELLURIUM.

Mention was made earlier of preliminary attempts to find the Hall effect in liquid tellurium. These attempts were repeated with the more elaborate apparatus but with substantially the same results. In spite of the greater precautions to eliminate disturbances it was found impossible to obtain consistent results. Transverse potential differences were obtained which were large compared to those which were obtained just previous to the melting of the metal; but these deflections were irregular in size and, at times, in direction. The author is of the opinion that the deflections noted were due chiefly, if not entirely, to mechanical motions of the liquid under the action of the magnetic field upon the primary current. Furthermore, that in the form of apparatus used, these disturbances would always be so large as to mask any Hall effect which might be present.

As far as the author is aware the Hall effect has never been found in an amorphous substance, with the exception of gases, mentioned previously. It would, therefore, be of as much interest to find it in a solid amorphous substance as in a liquid. It also seemed that, if tellurium could be obtained in an amorphous condition, the finely divided metallic precipitate, as obtained after the chemical purification, was certainly amorphous. Accordingly a specimen was prepared from some of this precipitate by pressure, sufficient to make a fairly compact mass but far from sufficient to cause the metal to flow. A Hall constant of $R = 60$ was found. A micro-photograph was then taken of some of the material with the result shown in Fig. 12. It is clear that the material used, in spite of its finely divided state, is crystalline and not amorphous.

In this connection it may be mentioned that the conviction has been growing in the mind of the author that the crystalline structure of a substance is not merely important but is necessary for the presence of the Hall effect, as we know it in general. It is true that it has been found in gases and it is possible that it exists to a slight extent in liquids; but such

Hall effects are simple and conform to simple theories, whereas in solids we are dealing with phenomena of great complexity the explanation of which must be on an entirely different basis so that it is a question whether they should even be looked upon as the same phenomena.

HEAT CONDUCTIVITY.

Measurements were made on the heat conductivity of the specimen last under investigation, both with and without a magnetic field. The

Fig. 12.

Microphotograph of Finely Divided Tellurium. (Magnification = 300 diameters.)

work was carried out with Dr. R. W. King[1] and by an ingenious method recently developed by him for finding the heat conductivity. This method consists, essentially, in measuring the velocity of propagation of a sinusoidal heat wave through the specimen. The method is particularly adapted for measurement in such a case as this. This work, which has been done only recently, must be considered as preliminary and it is hoped that the matter may be carried further at a later time. The results are as follows:

It has been assumed that the specific heat remains constant, that is, it is independent of the magnetic field. The last value for the conductivity was found after the magnetic field had been removed.

[1] King, PHYS. REV.

$t = 45.3°$, Density = 6.25, Spec. heat = .05.

Magnetic Field.	Coef. of Heat Conductivity.	Per Cent. Change of Conductivity.
0	.0145	
6650	.0120	19
0	.0140	

The increase of electrical resistance, or decrease in electrical conductivity, under the same magnetic field was about .4 per cent.

The only datum on this matter which has come to the attention of the writer is that given by Lloyd[1] in which he states that he found a decrease of 10 per cent. in the heat conductivity in a magnetic field of 4,700 gausses. This being a longitudinal effect we may assume that it follows the H^2 law. Using the figures above we have $19/(6{,}650)^2 = 43 \times 10^{-8}$. Using Lloyd's figures we have $10/(4{,}700)^2 = 45 \times 10^{-8}$.

SUMMARY.

The results of this experimental work lead to the following conclusions:

1. Up to 12,000 gausses the Hall and the Nernst constants show themselves to be nearly independent of the magnetic field, with indications of a slight maximum value in the neighborhood of 6,000 gausses. Within the errors of observation the Ettinghausen effect and the Leduc effect are proportional to the magnetic field.

2. The magnetic change of resistance shows itself closely proportional to the square of the magnetic field.

3. A dissymetry of the Hall effect was found to be proportional to the square of the field strength, *i. e.*, to the longitudinal effect, thus verifying Van Everdingen's explanation of the dissymetry.

4. A marked dissymetry in the longitudinal effect was found. This dissymetry is proportional to the field strength and, therefore, to the Hall effect. This dissymetry can be explained in a manner similar to Van Everdingen's explanation of the Hall dissymetry.

5. The value of the various constants, at room temperature, depends greatly upon the previous heat treatment. This is particularly true of the Hall constant for which, under certain conditions, enormous values —as high as 2,000—were obtained.

6. The Hall effect, initially positive, decreases rapidly with rise of temperature, reverses to a negative value at a temperature below 100° C., depending on the heat treatment, and reverses to a positive value again in the neighborhood of 240° C. An explanation can be given on the assumption that tellurium occurs in two crystalline forms which may be

called the α tellurium and the β tellurium. The α modification is stable below about 200° C. and the β modification is stable above this temperature. There is a large time lag in the transformation from the one form into the other which accounts for the great influence of the heat treatment.

7. The Ettinghausen effect and the Nernst effect increase quite rapidly with rise in temperature. The Nernst effect reaches a maximum at about 100° C. after which it decreases rapidly. There are indications that the Ettinghausen effect also reaches a maximum at this temperature and then decreases.

8. The resistance and the longitudinal effect decrease rapidly with rise in temperature but show no reversals and no discontinuities.

9. The Hall effect and the thermo-electric power with respect to temperature give the same form of curves, showing a very intimate relationship between the Hall effect and the thermo-electric power. By the choice of a new standard from which to make measurements the thermo-electric power has a double reversal at the same temperatures as for the Hall effect.

10. Attempts were made to detect the presence of the Hall effect in liquid tellurium but without definite results. Rather large potential differences were found but they were irregular in magnitude and direction so that it was concluded that the effects noted were due to mechanical motions of the liquid.

11. Measurements were made on the heat conductivity of tellurium, both with and without a magnetic field. A large decrease in the heat conductivity was found when in the magnetic field. This decrease was much greater than the decrease in electrical conductivity under the same conditions.

In conclusion I wish to express my thanks to the Rumford Committee, which bore part of the expense of this investigation. My thanks are also due to Professor Nichols and Professor Merritt for the continual interest and assistance which they have given to this work.

CORNELL UNIVERSITY, 1915.

THE EFFECT OF TEMPERATURE UPON THE COEFFICIENT OF ABSORPTION OF CERTAIN GLASSES OF KNOWN COMPOSITION.

BY K. S. GIBSON.

INTRODUCTORY.

THE effect of temperature upon the absorption spectra of various kinds of colored glass has been investigated by Houstoun[1] and by Gibbs.[2] Their results show that in general the absorption increases with temperature, though in some instances, in certain parts of the spectrum, it decreases. In some specimens, upon heating, the absorption bands were found to remain stationary, and in others to shift toward the red. In only one case, found by Gibbs, has a shift of the absorption band toward the violet been observed, and in this specimen a permanent change in the spectrum was produced. Usually there was a complete recovery upon coming back to the original temperature.

The purpose of this investigation has been to study the changes that take place in the absorption spectra of certain glass specimens between the temperatures of $-180°$ and $430°$ C. These glasses were kindly furnished by the Corning Glass Works. There are five of them, their color and material being listed as follows:

No.	Color.	Coloring Material.	Glass.	Thickness.
1	Red	Cadmium, selenium	Zinc	1 mm.
2	Orange	Cadmium, selenium	Non-lead	2 mm.
3	Light amber	Cadmium, selenium	Borosilicate	2 mm.
4	Lemon yellow	Cadmium sulphide	Zinc	2 mm.
5	Canary	Uranium	Lead	2 mm.

By mistake No. 5 was at first listed as Cd Se and hence was studied with the others. The first four comprise an interesting and instructive series since the edge of the absorption band is at a different position in the spectrum of each, though of the same general character. Conclusions may thus be drawn from a study of this series, which might not be possible with specimens of various composition whose absorption curves are entirely different in shape from one another.

[1] Houstoun, Ann. der Phys., 21, p. 535, 1906.

[2] Gibbs, R. C., PHYS. REV., Vol. XXXI., No. 4, p. 463.

APPARATUS.

These glasses were ground in the shape of circular discs about 22 mm. in diameter and from one to two mm. thick. The faces were highly polished and made parallel to within .01 mm. These precautions were found necessary in order to obtain the same and therefore the correct per cent. transmission when the specimen was moved around in its position.

To study the effect of heating, the glass N (Fig. 1) was placed between two iron washers and heated in the furnace H. A thin cylindrical shell

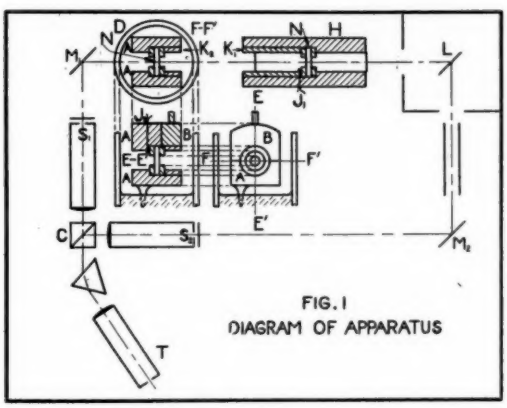


Fig. 1.

of iron K_1 kept the specimen and washers in position. The furnace was an iron core, hollowed out as indicated. Heating was produced by passing a current through wires wound on the outside. These wires were embedded in asbestos cement and the furnace then wrapped in many layers of asbestos paper, which prevented an excessive loss of heat by radiation. A piece of mica at each end prevented air currents and thus helped to keep the temperature on the inside steady. All temperatures were measured by means of a copper-advance thermo-junction which was inserted as indicated at J_1. This was used in the usual way with a potentiometer. It was calibrated by taking readings at the known temperatures of 0° and 100°, and at 232°, 327.5° and 419° C., the melting points of tin, lead and zinc respectively. At low temperatures it was calibrated by comparing it with a thermojunction whose calibration was known, readings being taken at a number of temperatures between 0° C. and the temperature of liquid air.

From the above readings a curve was drawn, and from this the potentiometer readings for any desired temperature could be obtained. The

accuracy of this calibration is such that the maximum variation from any of the temperatures as given is probably not more than two or three degrees.

To study the effect of cooling, apparatus was used which had been devised and constructed by Professor Gibbs for work at low temperatures. This consisted of a solid iron support A which could be lowered and clamped into position inside of a Dewar bulb D. This support was hollowed out and part of the upper half B was cut out and made removable. The glass N could then be lowered into its position between two washers and held in position by a cylindrical iron shell K_2. Then the cover B could be lowered into place. The liquid air was pumped into the bottom of the Dewar through a glass tube and the temperature varied by varying the amount of liquid air. An iron pointer fastened to the bottom of A helped to lower the temperature quickly and keep it steady. Windows of mica were not needed here as there were no convection currents in the air, and no trouble was experienced in keeping the temperature steady. The thermo-junction was inserted at J_2 as indicated. Precautions were taken to prevent dust from settling on the inside of the Dewar in the path of the light beam or upon the specimen during the observations. Also it was found necessary, in order to prevent condensation of moisture from the air on the outside of the Dewar, to fasten heating coils on each side about the places where the light entered and left.

The source of light used was an acetylene flame L whose pressure was kept constant by means of a water manometer. The light from this source, after passing through the specimen in the furnace or in the Dewar, was reflected by a mirror M_1 into the slit S_1 of one of the collimators of a Lummer-Brodhun spectrophotometer. The intensity of this light was compared by means of the Lummer-Brodhun cube C with the intensity of light from the same source L reflected by means of the mirror M_2 into the slit S_2 of the other collimator. A uniform contrast field was obtained by the use of ground glass screens placed in front of the slits. This field was viewed by the telescope T, used without the eye piece.

To exclude stray light, the acetylene flame and the spectrophotometer were boxed in and other screens used where needed, so that errors from this source were eliminated so far as the eye could detect.

During all observations the slits in the collimator S_1 and in the telescope T were kept constant at .80 mm., and the width of S_2 varied until a match was obtained. The amount of spectrum included by a slit of .80 mm. at wave-lengths .46μ, .56μ and .66μ is indicated at the bottom of each figure. A calibration curve was first obtained by taking observa-

tions throughout the spectrum with the specimen removed but everything else in position. By repeated trials and adjustments of apparatus, a curve was obtained which varied but little throughout the spectrum, which kept constant from week to week, and which was practically independent of the acetylene pressure over a considerable range, though as stated before the pressure was kept as nearly constant as possible. Thus the errors due to calibration were small. At least three settings of the slit S_2 were made for any particular wave-length, care being taken to avoid any lost motion in the screw. If these three did not agree closely, more were taken. This was almost always necessary at the red and violet ends of the spectrum.

If the average of the settings with the specimen in position is D, and the setting with the specimen removed is I (taken from the calibration curve), then D/I is the per cent. of the incident light transmitted. But since about 4 per cent. of the light incident on each surface of the glass is reflected at that surface, the true per cent. transmission P is approximately equal to $D/.96^2I = D/I'$.

The value of the coefficient of absorption K is derived as follows. If dI' is the change in intensity of light transmitted through a thickness dx, then dI' is proportional to $-dx$ and to I', the original intensity; *i. e.*, $-dI' = KI'dx$ where K is called the coefficient of absorption of the substance for any particular wave-length. From this

$$\int_{I'}^{D} dI'/I' = -\int_{0}^{x} Kdx,$$

$$\log D/I' = -Kx,$$

$$\log 1/P = Kx,$$

$$K = \frac{\log 1/P}{x},$$

where x is the thickness of the glass specimen. In computing K, the values of $\log 1/P$ were taken from a curve plotted between P and $\log 1/P$.

RESULTS.

In Figs. 2 to 9, the results of the investigation are shown graphically. In Figs. 2 to 6, the values of P, the per cent. transmission and of K, the coefficient of absorption are plotted against wave-lengths for various temperatures. In each figure, both for P and for K, there are seven curves corresponding to the following temperatures, with the two exceptions noted below.

Curve No. 1 was taken at −180°, No. 2 at −80°, No. 3 at +20°, No. 4 at 100°, No. 5 at 210°, No. 6 at 320°, and No. 7 at 430° C.

With specimen No. 3, Fig. 4, however, it happened that curve 2 was taken at −95° instead of −80° and in specimen No. 4, Fig. 5, curve 2

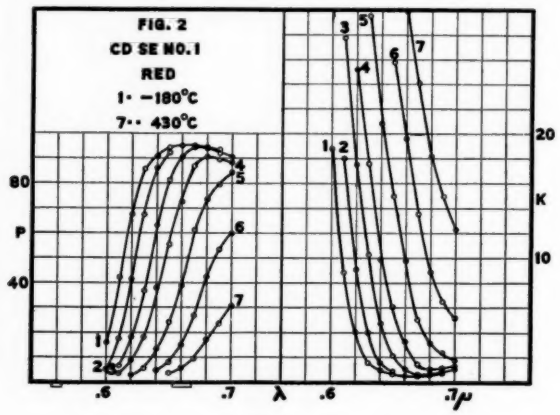


Fig. 2.

Glass No. 1. Cd, Se. Variation of the per cent. transmission P and of the coefficient of absorption K with wave-length λ at the temperatures −180°, −80°, +20°, 100°, 210°, 320° and 430° C.

was taken at −60° instead of −80° C. The values for 20° are the average of the values taken just before heating, and just before cooling. The cooling effect was studied about a year after the heating effect. In Fig. 2 all the curves are numbered. In the other figures curves 1 and 7 only are numbered.

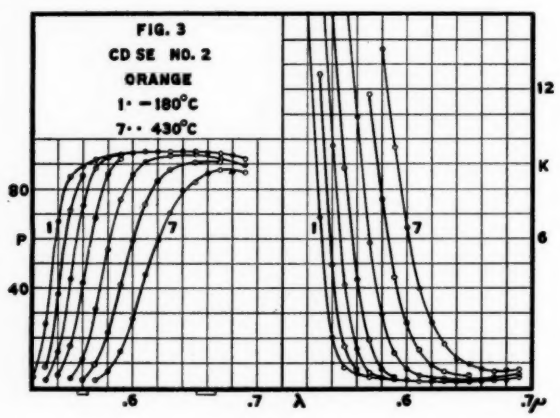


Fig. 3.

Glass No. 2. Cd, Se. Variation of the per cent. transmission P and of the coefficient of absorption K with wave-length λ at the temperatures −180°, −80°, +20°, 100°, 210°, 320° and 430° C.

In Figs. 7 and 8, values of K are plotted against temperature T for those wave-lengths which show the greatest changes. These curves are

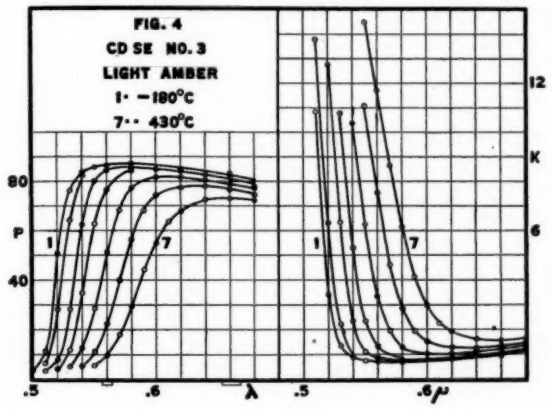


Fig. 4.

Glass No. 3. Cd, Se. Variation of the per cent. transmission P and of the coefficient of absorption K with wave-length λ at the temperatures −180°, −95°, +20°, 100°, 210°, 320° and 430° C.

for specimens Nos. 1 to 4 as indicated. In Fig. 9 are plotted values of K at the extreme temperatures, −180° and 430°, for the four *Cd* specimens.

Perhaps the most interesting and important result found in this in-

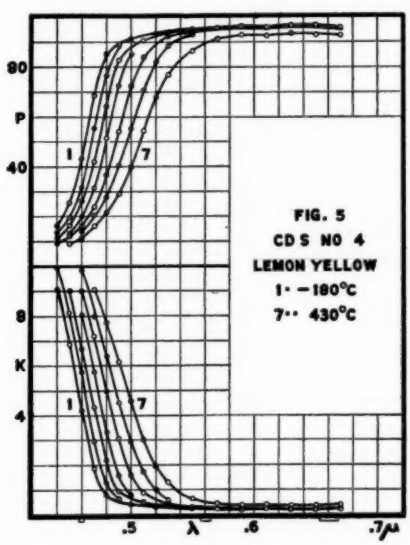


Fig. 5.

Glass No. 4. Cd S. Variation of the per cent. transmission P and of the coefficient of absorption K with wave-length λ at the temperatures −180°, −60°, +20°, 100°, 210°, 320° and 430° C.

vestigation is the enormous increase in the coefficient of absorption in certain parts of the spectrum. In the red glass for instance at certain

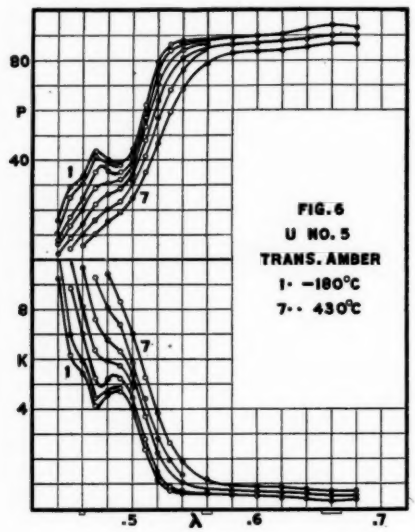


Fig. 6.

Glass No. 5. Uranium. Variation of the per cent. transmission P and of the coefficient of absorption K with wave-length λ at the temperatures −180°, −80°, +20°, 100°, 210°, 320° and 430° C.

wave-lengths, K is increased at 430° by more than fifty times its value at −180°; and what was nearly a transparent glass in the region of .66μ

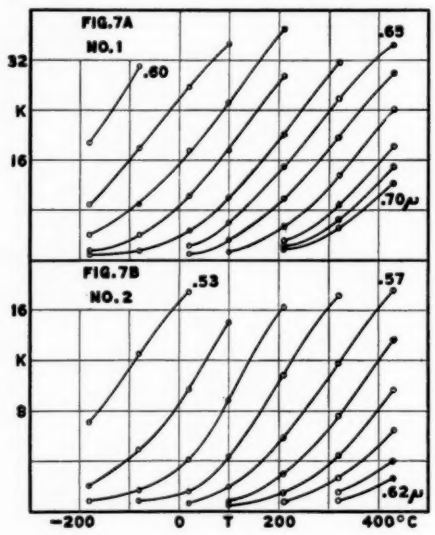


Fig. 7.

Glasses Nos. 1 and 2. Variation of the coefficient of absorption K with temperature T at certain wave-lengths.

became nearly opaque. In spite of these big changes, there was in all the specimens nearly a complete recovery after the heating; and after

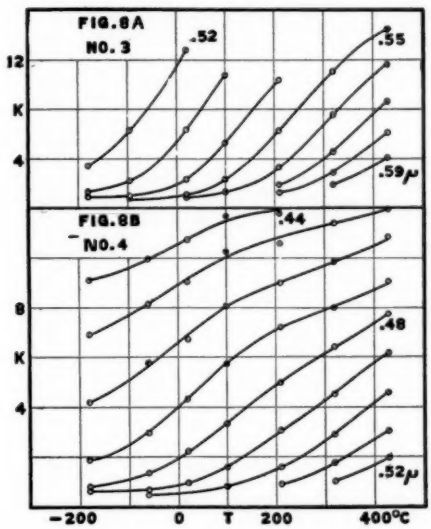


Fig. 8.

Glasses Nos. 3 and 4. Variation of the coefficient of absorption K with temperature T at certain wave-lengths.

cooling no change at all was found in the room temperature curves.

The biggest changes occur on the edge of the general absorption region,

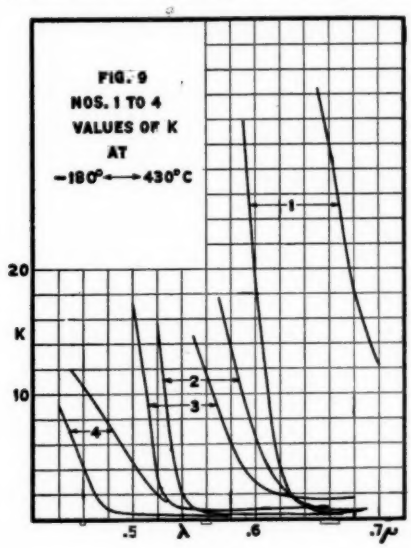


Fig. 9.

Glasses Nos. 1 to 4. Variation of the coefficient of absorption K with wave-length λ at the extreme temperatures, −180° and 430°, only.

and this results in some cases in a shift of the point of maximum per cent. transmission as can be seen from the curves. Also as might be expected, in some of the specimens there was a change in color, the orange glass becoming yellow at $-180°$ and turning to a brilliant red at 430°. The light amber glass became pink at 430°. The other specimens did not show marked color changes, though the red glass changed from a bright to a very deep red at 430°.

It is also interesting to notice (Fig. 9) that the edge of the absorption band is much sharper in the red glass than in the lemon yellow one, where the edge is in the violet, and that the curves for the other two specimens are intermediate in slope. But as the specimens are heated and the edge of the absorption band shifts toward the red, it becomes less sharp, though the difference is not great.

Also it will be noticed that the red specimen, which has the steepest curve, shows the greatest change in the value of K at different temperatures, the change becoming less and less in the other specimens as we go toward the violet.

A change in the per cent. transmission of "red pyrometer glass, presumably made with copper oxide" has recently been observed by Hyde, Cady and Forsythe.[1] Values of the coefficient of absorption at 20° and at 81° C., computed from their curves, show a change of the same order of magnitude as those noted above for the red specimen.

The specimen of canary glass containing uranium, No. 5, Fig. 6, though of different material and with a very irregular curve, yet shows the same effects upon change of temperature as the others. This glass is also interesting as showing how the absorption bands near the region of general absorption disappear upon heating. The specimen shows a green fluorescence, probably due to the absorption band at .49μ. It would be interesting to study the fluorescence and see if it disappeared at the same temperature as this absorption band.

CORNELL UNIVERSITY,
Sept., 1915.

[1] E. P. Hyde, F. E. Cady and W. E. Forsythe, PHYS. REV., p. 74, July, 1915, and Astrophysical Journal, Nov., 1915.

THE X-RAY SPECTRUM OF TUNGSTEN.

BY W. S. GORTON.

IN the work on the X-ray spectra of the elements, tungsten has certainly been used as frequently, with the possible exception of platinum, as has any other element but the results obtained by various workers do not agree very well. De Broglie[1] has photographed the spectrum of tungsten using a rotating crystal of rock salt as an analyzer. He gives two tables of lines, but the values given in the two tables differ considerably and, moreover, one table gives four lines and two bands while the other gives five lines and two bands. Herweg[2] finds three lines in the tungsten spectrum, while Moseley,[3] who has done much work in this direction reports only one line. He could, moreover, find no trace of the bands reported by de Broglie. Bragg,[4] who used an ionization method of detection (as have also Moseley and Darwin[5]) reports only one line, the wave-length of which differs considerably from the wave-length as given by Moseley. One would expect tungsten to have a spectrum at least as extensive as that found by de Broglie for, according to Moseley, the heavy metals in general have in their spectra five lines: α, β, γ, δ, ϵ in order of decreasing intensity. There is always a faint companion α' on the long wave-length side of α, a rather faint line ϕ between γ and β of the rare earth elements and a number of very faint lines of wave-length greater than α. All the workers in this field agree that the characteristic radiation of tungsten is rather weak. Now all previous work seems to have been done with X-ray tubes excited by induction coils; consequently, it seemed very probable that with the use of more powerful apparatus, such as the author had at his disposal, more lines could be detected and the ones already found confirmed.

In the present work a Coolidge tube was used as the source of X-rays and the tube was excited by a 10 K.W. interrupterless generator of the Snook Roentgen Co. This machine consists of a 10 K.W. step-up transformer and a synchronously revolving switch which rectifies the high tension E.M.F. This combination of tube and generator is very convenient for X-ray work as it will run for long periods of time without

[1] De Broglie, Comptes Rendus, 157, 1413, 1913; 158, 177, 1914.
[2] Herweg, Verh. d. D. Phys. Ges., 16, 73, 1914.
[3] Moseley, Phil. Mag., (6), 26, 1024, 1913; 27, 703, 1914.
[4] W. H. Bragg, Proc. Roy. Soc., 89A, 246, 1913.
[5] Moseley and Darwin, Phil. Mag., (6), 26, 210, 1913.

the slightest attention, meanwhile maintaining all conditions perfectly constant.

The spectrometer used was of the type in which slit and detecting device are on the circumference of a circle through the center of which passes the face of the analyzing crystal; the face of the crystal is perpendicular to the plane of the circle. This arrangement has the advantage, as shown by Bragg,[1] that the position of any line is independent of the position of the crystal. In the present work the detecting device was a photographic film bent to the radius of the circle mentioned. On the table which carried the crystal was a small brass cone, the axis of which coincided with the axis of the spectrometer. The shadow of this cone was cast on the film and defined the point on the film diametrically opposite the slit. This device enabled all measurements to be carried out on the film itself and obviated the necessity of an accurately graduated circle which is necessary to determine the position of the plate-holder if plates be used. A circle graduated to degrees was provided for setting the crystal. Fig. 1 shows

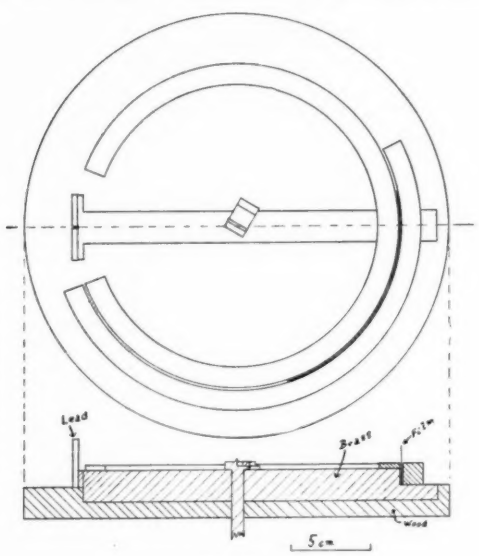


Fig. 1.

the general plan of the spectrometer and Fig. 2 the design of the crystal holder. The width of the slit was $\frac{1}{4}$ mm., the material of the jaws being $\frac{1}{8}$ in. (3 mm.) lead. The photographic film was inclosed in a black paper shield and the whole spectrometer was protected by a covering of $\frac{1}{8}$ in. sheet lead.

In the present investigation the crystal was kept stationary during the exposure. In some previous photographic work, notably that of de

[1] W. H. and W. L. Bragg, Proc. Roy. Soc., 88A, 428, 1913.

Broglie, the crystal was kept in rotation during the exposure. This latter procedure has the advantage of recording all the lines on the film simultaneously but requires as a rule long exposures, sometimes as much as six hours. In the present work long exposures were inexpedient for various reasons, and so all photographs were made with the crystal at rest. This method records only a small portion of the spectrum at any one exposure but experience has shown that, in the first order, exposures made with the particular crystal used in the present work, in successive positions one degree apart, will record all of the spectral lines. The reason for this may readily be seen by reference to Fig. 3. The X-rays

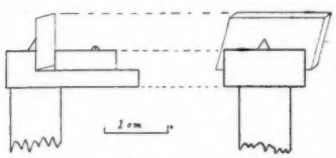


Fig. 2.

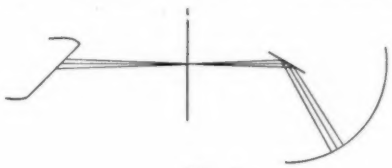


Fig. 3.

come not from a point on the anti-cathode of the bulb but from an extended area. Thus, different rays strike the crystal at different angles, and, as a consequence, all rays having wave-lengths lying within a certain range affect the film. The present method has the further advantage, as may readily be seen, that very faint lines can be detected much more easily than with a rotating crystal unless extremely long exposures are used. In the present work the usual length of exposure was five minutes. Fairly good results were obtained, however, with exposures as short as one minute, while no gain was experienced by increasing the exposure to fifteen minutes.

The usual current through the X-ray bulb was 0.020 ampere and the parallel spark gap was 4 in. (10 cm.), corresponding to a maximum potential difference on the tube of 76,000 volts. No essential change was produced by raising the gap to 8 in. (20 cm.) (122,000 volts). The analyzing crystals were calcite and rock salt, two of each kind being used. Calcite was used because it is comparatively easy to get a calcite crystal which gives clear, sharp lines when used as an analyzer of X-rays. It is not so easy to get a good rock salt crystal but rock salt was also used in the present work because most of the previous workers have used rock salt. It gives lines darker but not quite so sharp as those of calcite. The two calcite crystals gave equally good results. One of the rock salt crystals, however, gave much better definition than the other. The crystal giving the better definition was the one which had the optically better surfaces. The crystals were bounded entirely by cleavage planes. The dimensions of the crystals were $2.2 \times 0.8 \times 0.3$ cm. in the case

of the rock salt, and 1.5 × 0.9 × 0.3 cm. in the case of the calcite. These dimensions are much less than those of the crystals used in most of the previous investigations on the subject. This has the disadvantage of allowing a less extended range of wave lengths to be recorded for any one position of the crystal but makes it far easier to find a suitable crystal.

The results of the work are given in Table I. The values of the wave-length λ were calculated from the formula:

$$n\lambda = 2d \sin \theta$$

where n is the order of the spectrum (always unity in the present work), d the distance apart of the atomic planes and θ the angle between the face of the crystal and the beam of X-rays. The value of d for the cubic (100) face of rock salt has been given by W. L. Bragg[1] as 2.814×10^{-8} cm. The value of d for the rhombohedral (100) face of calcite was calculated from the results of the present work to be 3.028×10^{-8} cm. The measurement of θ for each line was accurate to one-third of one per cent. As each value of θ given in the tables was the average of meas-

TABLE I.

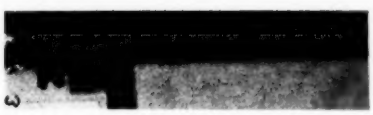
Lines.		Calcite Analysis.		Rock Salt Analysis.		Average Value of λ×10⁸
Name.	Strength.	θ	λ × 10⁸	θ	λ × 10⁸	
a_1	faint	14.10°	1.474	15.21°	1.477	1.476
a	strong	14.01	1.466	15.10	1.465	1.466
b_1	faint	12.34	1.294	13.28	1.290	1.292
b_2	very faint	12.24	1.283	13.17	1.283	1.283
b	strong	12.14	1.273	13.11	1.277	1.275
c	faint	11.97	1.257	12.88	1.255	1.256
d	strong	11.77	1.235	12.70	1.238	1.237
g	strong	10.39	1.092	11.21	1.095	1.094
h	medium	10.06	1.057	10.83	1.057	1.057
k	faint	9.75	1.026	10.48	1.024	1.025

urements made on several films, the values of λ may be considered accurate to one-fifth of one per cent. The lines are classified, according to intensity as being strong, medium, faint, or very faint. Some of the lines are too faint to show when reproduced but many show up well. Several prints of the original films are shown in Plate I. An effort was made to obtain prints in which the very faint lines would be intensified, by the process of photographing the films using a slow plate and under-exposing it, but the results were not noticeably better than those shown in Plate I. No retouching of any sort has been done. The hazy bands adjacent to some of the lines are due to the general radiation from the tube.

The number of lines found in the present investigation is larger than

[1] Bragg, Proc. Roy. Soc., 89A, 248, 1913.

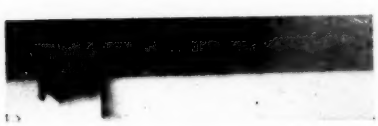
Calcite. Lines a_1 and a.



Rock salt. Lines a_1 and a.

Calcite. Lines b_1, b_2, b, c, and d.

Rock salt. Lines b_1, b_2, b, c and d.



Calcite. Lines g and h.

Rock salt. Line g.

Calcite. Lines h and k.

Rock salt. Lines g and h.

Rock salt. Line k.

Fig. 5.

X-ray Spectrum of Tungsten.

W. S. GORTON.

has been hitherto reported. Moseley[1] reported only one line for tungsten; this was the α line. He gave the wave-length as 1.486×10^{-8} cm. This is probably the a line of the present work. The β and γ lines, according to Moseley's formula, should have the wave-lengths 1.286×10^{-8} and 1.248×10^{-8} respectively. The ϕ line is between β and γ. The b, d, and c lines seem most nearly to fill the calculated places of the β, γ, and ϕ lines respectively. No lines having wave-lengths greater than that of $\alpha'(a_1)$ were found. De Broglie[2] in the latter of his two tables (which differ considerably) reports the lines; $\theta = 11° 14'$ s., $12° 44'$ s., $12° 55'$ f., $13° 08'$ s., and $15° 09'$ s., rock salt being the crystal. These values agree very closely with those for the g, d, c, b, and a lines of the present article. Since the completion of the present work but before the writing of this paper, Barnes[3] has given the results of an investigation carried out by him using a rotating rock salt crystal as analyzer. He reports the following lines:

θ	$\lambda \times 10^8$	Intensity.
15° 13′	1.477	strong
13° 29′	1.312	weak
13° 19′	1.296	strong
13° 07′	1.277	weak
12° 55′	1.258	strong
11° 24′	1.113	strong
11° 05′	1.082	weak

These values seem to fit best the a, b_1 b, c, d, g, and h lines but the values of θ are uniformly higher than those found by the author. The a_1, b_2, and k lines were apparently not found.

It is important to inquire into the cause of the discrepancies between Barnes's results and those of the author. While the results of de Broglie do not differ from the author's by more than 0.3 per cent., Barnes's results are uniformly higher by from 1.0 to 2.3 per cent. The difference is not due to any differences in the velocities of the cathode rays which conceivably might cause a difference in the wave-lengths of the characteristic radiation; the author has tested this point. Moreover, no such difference as one per cent. would be expected. The tubes used in the investigations were both Coolidge tubes; consequently, the cause is not to be sought in any variation or impurity in the material of the cathode. This leaves instrumental errors as the only other likely cause. Barnes does not give a diagram of his apparatus but the arrangement, as well as can be made out from his description, is that represented in Fig. 4.

[1] Moseley, *l. c.*

[2] De Broglie, *l. c.*

[3] Barnes, Phil. Mag. (6), 30, 368, Sept., 1915.

(This arrangement has also been used by de Broglie.) S represents the slit (0.5 mm. in width), O the axis of the spectrometer, and PP' the photographic plate. His procedure was to make an exposure with the crystal

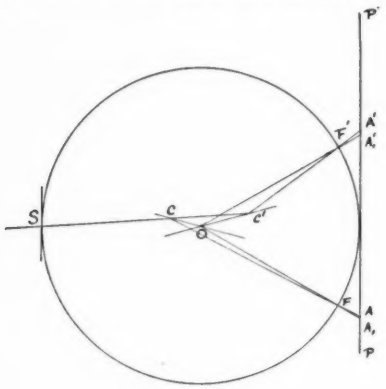


Fig. 4.

rotating slowly in the neighborhood of the position represented by OC', then to change over to OC and make a second exposure, thus producing two lines on the plate. This method is bad because it is necessary to use a very narrow beam of X-rays in order to get sharp lines. All the reflected beams of a certain wave-length pass through, say, either F or F'. If we have a very narrow beam of rays passing through O, this will produce lines at A_1 and A_2'. A beam SCC' would produce lines at A and A'. Consequently, if a beam of rays having an angle of several degrees is used, broad diffuse lines will result making measurement difficult. It is easily seen, too, that the position of the maximum intensity in the lines is dependent on the distribution of intensity in the incident beam of X-rays. Any variation in the velocity of rotation of the crystal would likewise have an effect on the distribution of intensity in the lines. None of these objections apply to the present work, for the photographic film was everywhere on the circumference of the circle. The device of the small brass cone for marking on the film the intersection of the line SO with the circle does not introduce any error. Films exposed, as in Barnes's work, so as to produce symmetrically placed lines gave the same results as those of Table I. within the limit of error of the method.

The conclusion of the present work is that tungsten shows the same general type of spectrum as do the rest of the heavy metals. The number of lines here reported is greater than has been found hitherto; it is possible that with much longer exposures still further additions to the number may be made.

JAMES BUCHANAN BRADY UROLOGICAL INSTITUTE,
JOHNS HOPKINS HOSPITAL,
BALTIMORE.

THE TEMPERATURE COEFFICIENT OF CONTACT POTENTIAL.

BY K. T. COMPTON.

FROM a consideration of the conditions of statistical equilibrium of the electrons inside and outside different metals in contact, Professor Richardson[1] has derived the equation

$$V_m - V_s = \frac{1}{e}(\phi_m - \phi_s) + P \qquad (1)$$

for the contact difference of potential between the metals m and s. In this equation ϕ is the difference between the average potential energy of an electron inside and outside the metal. The latent heat of evaporation of an electron w which has been directly measured in several cases differs from ϕ only by the addition of a very small term denoting the difference between the rates of transfer of energy per electron by currents inside and outside the metal, if such a difference exists. This quantity, introduced, by Professor Richardson, appears to define one of the most important characteristics of the metal, since it is the measure of the work required to extract an electron from the metal. w has been measured directly[2] for platinum, osmium and tungsten and calculated for a large number of metals from data of thermionic[3] and photoelectric[4] emission.

The last term P which represents the Peltier difference of potential between the metals is comparatively very small. Neglecting this term, equation (1) is supported by such evidence as we have on the subject. A direct experimental test of the complete equation appears impossible owing to the extreme smallness of P in comparison with the limits of accuracy attainable in measurements of w. Equation (1) may, however, be transformed[5] to involve only the first and last terms, giving the equation

$$\frac{\partial}{\partial T}(V_m - V_s) = \frac{P}{T}, \qquad (2)$$

[1] "Electron Theory of Matter," pp. 455, 456.

[2] O. W. Richardson and H. L. Cooke, Phil. Mag., 20, p. 173, 1910; 21, p. 404, 1911; 25, p. 624, 1913; 26, p. 472, 1913; H. A. Wilson, Phil. Trans., A, 202, p. 243, 1903.

[3] O. W. Richardson, Phil. Trans., A, 201, p. 497, 1903.

[4] O. W. Richardson and K. T. Compton, Phil. Mag., 24, p. 575, 1912.

[5] "Electron Theory of Matter," p. 459 (37).

which should be capable of experimental test.[1] The object of this paper is to discuss the results of attempts to test this equation.

According to equation (2) we should expect the temperature coefficient of contact difference of potential to be very small. For iron and bismuth and iron and nickel, for instance, equation (2) leads to the values, at 50° C.,

$$\frac{\partial}{\partial T}(V_{Fe} - V_{Bi}) = 0.0000887 \text{ volt per degree,}$$

$$\frac{\partial}{\partial T}(V_{Fe} - V_{Ni}) = 0.0000324 \text{ volt per degree.}$$

For none of the common metals are the thermoelectric powers larger than these. Thus on changing the temperature from 0° C. to 100° C. we should expect to observe variations in the contact differences of potential of approximately 0.00887 and 0.00324 volt respectively, which are large enough to measure with suitable apparatus.

We have both direct and indirect experimental evidence on which to base a test of the theory. From certain photoelectric[2] and thermionic[3] experiments we may conclude that the temperature coefficient of contact difference of potential is less than the influence of disturbing factors and experimental error. But as the magnitude of these uncertainties considerably exceeds that of the effect under consideration we can obtain no positive information from this source.

Such direct experiments as have heretofore been made lead to values of the temperature coefficient which are entirely too large to be consistent with equation (2). Probably the most reliable results have been obtained by Erskine-Murray[4] and Burbridge,[5] who found temperature coefficients of contact potential varying between -0.0022 and 0.0043 volt per degree for different metals. These results are of the order of a hundred times too large to fit equation (2) and the measured values bear no obvious relation to the thermoelectric powers. Accurate measurements are difficult to make owing to the smallness of the effect in com-

[1] It is perhaps worth while to call attention to the recent criticism of the reasoning employed by Professor Richardson by W. Schottky, Verh. d. D. Phys. Ges., 17, p. 109, 1915. This criticism is based largely on the results obtained by Schottky when he applies the energy principle to a thermodynamic cycle similar to that treated by Richardson and obtains an equation inconsistent with the corresponding one derived by Richardson. Schottky, however, seems to have misapplied the energy principle when he places the total heat absorbed equal to zero in the reversible cycle which is not isothermal (Equation (6), p. 113). When this is corrected his results are not inconsistent with those given by Richardson.

[2] R. A. Millikan and G. Winchester, Phil. Mag., 14, p. 188, 1907.

[3] W. Schottky, Ann. d. Physik, 44, p. 1011, 1914.

[4] Phil. Mag., 45, p. 424, 1898.

[5] PHYS. REV., 2, p. 183, 1913.

parison with superposed effects due to insulation charges, time changes and oxidization. Yet there seems to be no doubt but that the experimental results are not in accord with the theory, assuming the usual interpretation of these results to be correct.

Apparatus.—The experimental measurements thus far made have been by some form or modification of the variable condenser method. It seemed worth while to make measurements by the ionization method, in which the air between two plates is ionized by γ rays and the potentials of the plates so adjusted by a potentiometer that no current passes between them, the applied difference of potential being then equal to the contact difference of potential. As compared with the older method, this method has the advantages of greater accuracy, elimination of static charges developed by moving parts and quickness and convenience in manipulation.

A cross section of the apparatus and a diagram of the connections are shown in Fig. 1. *NN* and *FF* are the opposing nickel and iron faces,

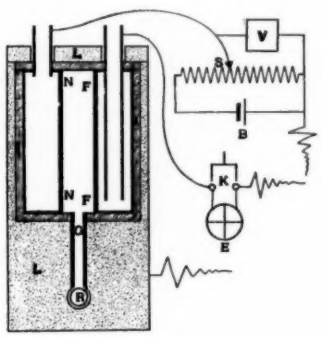


Fig. 1.

respectively, of two hollow metal boxes, each about $6\times4\times\frac{1}{2}$ inch. These boxes are surrounded by hard rubber insulation *I* and fit in the cavity of the lead block *LL*. A tube of radium was placed at *R* so that the γ rays passing up through the fan-shaped groove *G* ionized the air between the plates *NN* and *FF*. Two tubes passing into each box served as intake and overflow for the stream of water which was used to regulate the temperature of the plates. This device, while clumsy, was preferable to heating in an oven because it permitted very rapid variations in the temperature. One box was connected to the potentiometer and subdivided millivoltmeter and the other to one pair of quadrants of an electrometer. The sensitiveness of the apparatus was such that the contact difference of potential could be measured accurately to the ten thousandth of a volt.

Time Changes.—It was first planned to polish the plates (with emery paper, then glass paper, then clean cotton), place them in position immediately and measure the contact difference of potential at different temperatures within a few minutes after polishing. When this was attempted, however, the measurements were very erratic and bore no resemblance to the true contact difference of potential. This effect did not disappear until four or five hours had elapsed after polishing and reappeared whenever the apparatus was slightly jarred or disturbed. Various tests made it evident that frictional charges, probably on the rubber insulation, were responsible for this spurious effect. Inability to avoid them when putting the boxes in place or polishing them in position made it necessary to wait several hours after polishing before making the desired measurements. During this interval as well as later the value of the contact difference of potential changed with time, the iron becoming more electronegative as is shown by Fig. 2. The solid

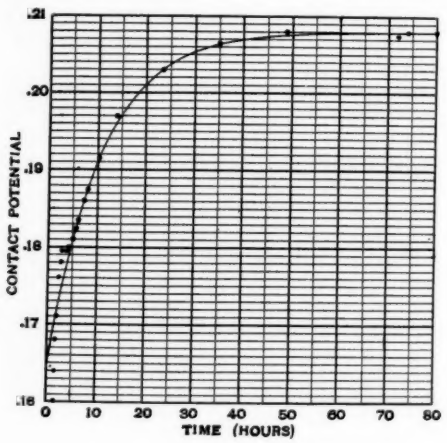


Fig. 2.

curve is a true logarithmic curve whose equation is

$$V_\infty - V = (V_\infty - V_0)e^{-kt} = (0.2080 - 0.1646)e^{-0.0925t} \qquad (3)$$

The experimental readings beyond five hours from the time of polishing fall almost exactly on the curve. The extreme regularity of the curve proves an accuracy of the experimental arrangement beyond anything hitherto attained in such measurements. Other similar tests yielded curves with the same values (approximately) of V_∞ and k but the values of V_0 varied somewhat.

The significant feature of these results is the fact that the iron became continually more electronegative with respect to nickel. This was

probably due to oxidation of the iron—an explanation supported by equation (3) which is of the form typical of chemical reactions of this kind. This oxide film, however, must have been extremely thin since the surface of the iron appeared as brightly polished at the end as at the beginning of the test.

The Temperature Coefficient of Contact Difference of Potential.—In view of these results the effect of temperature was tried only after the initial erratic variations had subsided and usually after the lapse of an interval of about twenty-four hours from the time of polishing. In various tests the temperature was varied within the interval 20° C. to 60° C. with the following results:

0.00216 volt per degree.
0.00154
0.00166
0.00113
0.00177
Mean = 0.00165 volt per degree.

While the large variations in these results indicate the effect of some disturbing factor, their general indication is plain. They are in good accord with the results obtained by the other method and are about fifty times as large as the theoretical coefficient deduced from equation (2).

Discussion.—There are two alternatives in interpreting the bearing of these results. Either equation (2) and therefore equation (1) does not conform to the facts or else what is actually measured is not the real contact difference of potential between the metals. Various lines of evidence support this second alternative. The rapid formation of an oxide film, very thin yet sufficient to alter the normal contact difference of potential, has occurred during the progress of all experiments of this sort. Thus we actually measure the contact difference of potential between opposing oxide surfaces (possibly so thin that the effects of metal and oxide superpose), so that we should expect to find temperature coefficients equal to or largely affected by the thermoelectric powers of the oxides. It has been recently shown by Bidwell[1] that the metallic oxides in general possess extremely high thermoelectric powers, some of them being sufficiently large to account for the observed values of the temperature coefficient of contact difference of potential by the theory expressed by equations (1) and (2).

It is possible that surface layers of a gaseous nature contribute to increase the variation of surface potential with temperature. If this were a predominating factor, however, we might expect a "lag" in

[1] PHYS. REV., 3, p. 204, 1914.

the potential change as the temperature is varied. No certain indication of such a lag was detected in these experiments.

Recently Professor Richardson[1] has shown that the presence on metals of surface films with large thermoelectric powers would account for certain peculiarities in the thermionic emission from metals.

Thus the status of the problem appears to be that no certain test of equation (2) has yet been made. The suggested explanation of the experimental results is certainly true to some extent but whether or not the entire discrepancy between theory and experiment may be thus accounted for is a question which at present cannot be answered. Preparation of surfaces and measurements in extremely high vacua, as were carried on successfully by Hennings[2] and Kadesch[3] can alone lead to a reliable test of the validity of equation (2).

The measurements described above were made in the physical laboratory of Reed College with the assistance of Mr. Ellis Jones of the senior class. I take pleasure in thanking him for his aid and for valuable suggestions.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

[1] Roy. Soc. Proc., A, 91, p. 524, 1915.
[2] PHYS. REV., 4, p. 228, 1914.
[3] PHYS. REV., 3, p. 367, 1914.

ON THE EFFECT OF GENERAL MECHANICAL STRESS ON THE TEMPERATURE OF TRANSITION OF TWO PHASES, WITH A DISCUSSION OF PLASTICITY.

BY P. W. BRIDGMAN.

THIS note is to present a thermodynamic formula of considerable generality, and to discuss some of its special cases. The need for such a formula arose in connection with experiments on the effect of high pressures on melting points and polymorphic transitions.[1] In these experiments the specimens were placed in open containing vessels of steel, which may be expected to offer some restriction to the free propagation of changes of hydrostatic pressure throughout the mass of the specimen. The question at issue was: what is the effect on a transition (or melting) point of unknown extra stresses not hydrostatic in nature? It was a surprise to me, after a careful search, to find that this problem has received very meager attention, although it is one capable of solution by ordinary thermodynamic methods. For instance, Voigt's encyclopædic work on "Krystall Physik" does not mention the problem, although it contains numerous examples of the use of the thermodynamic potential for solid bodies under strain. Formulas have, however, been given by James Thomson[2] and Gibbs,[3] among others, for the restricted case of a fluid in contact with an isotropic solid under elastic stress.

The conditions to which the general formula applies are as follows. Two phases of a pure substance, either gaseous, liquid, or crystalline solid, are initially in equilibrium under a hydrostatic pressure p and at absolute temperature θ_0. The two phases are in contact across a membrane of such a nature as to be permeable to the reacting phases, so that the transition from one phase to the other may run across the membrane, but such that it may support a difference of stress between the two sides, so that the normal component of stress on the two phases on opposite sides of the membrane need not be the same. A mechanical stress system, ${}_1X_x$, ${}_1Y_y$, ${}_1Z_z$, ${}_1Y_z$, ${}_1Z_y$, ${}_1X_y$, in addition to the hydrostatic pressure is applied to the phase (1), and a different stress system ${}_2X_x$, ${}_2Y_y$, etc., to the second phase. The *total* normal stresses (including the original

[1] P. W. Bridgman, Proc. Amer. Acad., 47, 345 and 439, 1912; 51, 53, 1915. PHYS. REV., N. S., 3, 126 and 163, 1914; 6, 1 and 94, 1915.

[2] James Thomson, Phil. Mag. (4), 24, 395.

[3] J. Willard Gibbs, Scientific Papers, vol. 1, p. 184.

hydrostatic pressure) across the surfaces of separation are now ${}_1N_\nu$, and ${}_2N_\nu$. In accordance with the usual practice of elasticity, the stress is considered positive if a tension. It is required to find the change of temperature τ necessary to bring the phases into equilibrium again across the surface of separation. The formula follows.

$$\tau = \frac{W_1 + \frac{1}{3}\left(\frac{\partial v_1}{\partial p}\right)_\tau ({}_1X_x + {}_1Y_y + {}_1Z_z)(p + {}_1N_\nu) - v_1({}_1N_\nu + p) - W_2 - \frac{1}{3}\left(\frac{dv_2}{\partial p}\right)_\tau ({}_2X_x + {}_2X_y + {}_2Z_z)(p + {}_2N_\nu) + v_2({}_2N_\nu + p)}{\frac{\lambda'}{\theta_0} + \left(\frac{\partial v_2}{\partial \tau}\right)_p \left\{\frac{1}{3}({}_2X_x + {}_2Y_y + {}_2Z_z) - p - {}_2N_\nu\right\} - \left(\frac{\partial v_1}{\partial \tau}\right)_p \left\{\frac{1}{3}({}_1X_x + {}_1Y_y + {}_1Z_z) - p - {}_1N_\nu\right\}}.$$

This formula is rigorously exact within the limits over which the coefficients remain constant, but the following approximation is good to small quantities of the first order:

$$\tau = \frac{\theta_0}{\lambda}\left[W_1 + \frac{1}{3}\left(\frac{\partial v_1}{\partial p}\right)_\tau ({}_1X_x + {}_1Y_y + {}_1Z_z)(p + {}_1N_\nu) - v_1({}_1N_\nu + p) - W_2 - \frac{1}{3}\left(\frac{\partial v_2}{\partial p}\right)_\tau ({}_2X_x + {}_2Y_y + {}_2Z_z)(p + {}_2N_\nu) + v_2({}_2N_\nu + p)\right].$$

The following additional terms used in the formula need explanation. λ is the heat absorbed (in the appropriate mechanical units per gm. of substance) when (2) changes to (1) at p, θ_0, and λ' is the corresponding heat of transition under equilibrium conditions under the altered stress at $\theta_0 + \tau$. W_1 is the work done by the stress system ${}_1X_x$, ${}_1Y_y$, etc., when applied isothermally to ONE GRAM of the phase (1), and similarly for W_2. W is to be calculated by the ordinary rules; in the case of a solid it may be found accurately enough by supposing the extra stress system applied to the phase at $p = 0$. It is to be noticed that because of the conditions of mechanical stability, W is essentially positive. $(\partial v/\partial p)_\tau$ is the " compressibility " of 1 *gm.* of the substance, and $(\partial v/\partial \tau)_p$ the " dilatation " of 1 gm.

It is easy to find the change in the latent heat under the changed conditions of equilibrium.

$$\Delta\lambda = \lambda' - \lambda = \frac{\tau}{\theta_0}\lambda + \tau({}_1\gamma_X - {}_2\gamma_X) + \theta_0\left(\frac{\partial v_1}{\partial \tau}\right)_p \left[\frac{{}_1X_x + {}_1Y_y + {}_1Z_z}{3}\right] - \theta_0\left(\frac{\partial v_2}{\partial \tau}\right)_p \left[\frac{{}_2X_x + {}_2Y_y + {}_2Z_z}{3}\right].$$

${}_1\gamma_X$ and ${}_2\gamma_X$ are the specific heats under constant stress.

The formulas were derived by ordinary thermodynamic methods; it is hardly worth while to reproduce the wearisome details. The method is to carry the substance around a complete cycle, writing down the two conditions that the total change of energy and of entropy of the cycle shall be zero. The changes of energy and of entropy of the two phases separately were obtained from Voigt's general thermodynamic potential for solids under stress. It is important to notice that we cannot in this general case write down the conditions of equilibrium by demanding that the thermodynamic potentials of the two solid phases be equal, as we can when dealing with fluid phases by using the potential $Z = E + pv - \theta s$. The thermodynamic potential as usually given for elastic solids is good only within the range of the small strains contemplated by the theory of elasticity, and is not good for the comparatively large changes of volume involved in a transition. It probably would not be difficult to extend the thermodynamic potential for solid bodies so as to attain this greater generality, but it was not necessary for the purpose in hand.

The formulas in the form given above apply only to homogeneous isotropic solids, or more generally to crystalline solids characterized by only one constant of thermal dilatation. The extension is immediate, however, to the most general crystalline solid with its 28 constants, comprising 21 elastic constants, 6 thermal expansion constants, and one specific heat. The 21 elastic constants are buried in the expression for W. The only formal change necessary is to replace, wherever it occurs,

$$\tfrac{1}{3}(\partial v/\partial \tau)_p[X_x + Y_y + Z_z] \text{ by } a_1X_x + a_2Y_y + a_3Z_z + a_4Y_z + a_5Z_x + a_6X_y,$$

where the "a's" are the six constants of thermal expansion. This produces no change in the approximate value for τ, but does enter the formula for $\Delta\lambda$.

It is evident that by a double application of the formula the still more general case may be treated of two phases initially in equilibrium under any stress system not hydrostatic. It is not worth while to further complicate matters by giving a single formula which shall apply to this general case.

SPECIAL CASES.

1. If the stress applied to the two phases is the same increment of hydrostatic pressure dp, the expression immediately reduces to Clapeyron's equation, as it should, by putting ${}_1N_\nu = {}_2N_\nu = -(p + dp)$; ${}_1X_x + {}_1Y_y + {}_1Z_z = {}_2X_x + {}_2Y_y + {}_2Z_z = -3dp$.

2. If the pressure on (1) is left unaltered and the stress on (2) is raised

to the hydrostatic pressure $p + dp$, we find immediately

$$\tau = -\frac{\theta_0}{\lambda} v_2 dp.$$

This is the well-known expression for the depression of the transition point by a pressure exerted on one phase only. It has been discussed by Planck, Poynting, Ostwald, Tammann, Lewis, and has recently been made the basis of a theory of plasticity by Johnston. We will return to this matter.

3. The formula for τ contains a theorem by its very form; the tangential stress on the surface of separation does not enter. The transition temperature of two phases under a given stress is therefore the same across all planes over which the normal stress is the same, and is not affected by the tangential stress at the surface of separation. A special case of this is that if shearing stresses are applied to two opposite faces of a cubical solid in equilibrium with a liquid or another solid the transition point is depressed by the same amount on all six faces of the cube, irrespective of whether these are the faces to which the shearing stress is applied or not.

4. Consider now the problem of the introductory paragraph for the case of a melting solid. A liquid (1) and a solid (2) in the form of a uniform cylinder are in equilibrium at p, θ_0. A mechanical tension is applied to the solid. We have to consider two faces of the solid, that freely exposed to the liquid, and that where the tension is applied. At the free surface we put

$$_1N_\nu = {}_2N_\nu = -p,$$

and find

$$\tau = -\frac{\theta_0 W_2}{\lambda},$$

a result independent of the initial pressure. The freezing point is therefore lowered, and the solid melts at the unstressed surface. It is to be noticed that W varies as the square of the applied stress, but it is not necessary for this reason to restrict the *stresses* to which the formula is applicable to small quantities of the first order. It is only necessary that the strains produced by the stresses remain small. Thus for steel, a stress as high as the elastic limit produces a strain of only 0.001.

At the stressed surface, if we suppose the membrane such that the solid would melt to a liquid at normal pressure p, we find,

$$\tau = \frac{\theta_0}{\lambda} v_2 X_x$$

or the melting point is raised, and no transition takes place at this surface, unless there is liquid present to freeze to the solid.

5. Imagine a cylinder of solid at its melting point and in equilibrium with it at one end only the liquid. Additional hydrostatic pressure dp is applied to the liquid, producing in the solid a one sided stress ${}_2X_x = -dp$. The normal stresses in solid and liquid across the surface of separation are in this problem equal. We find that at the surface of separation the melting point is raised by

$$\tau = \frac{\theta_0}{\lambda}(v_1 - v_2)dp,$$

and at the free surface it is depressed by the same amount as in the preceding problem. At the stressed surface the change of melting point is exactly the same as if the entire solid were subjected to the increment of hydrostatic pressure dp.

This has application to problems like that of a weighted wire melting its way through a block of ice, or the melting produced under the runners of a sleigh by its own weight. The usual treatments are faulty in that they assume hydrostatic pressure in the solid, whereas the stresses in these cases are not hydrostatic pressures, but are one-sided stresses to which the usual Clapeyron's equation does not apply. The above discussion shows, however, that immediately at the point where the pressure is applied, the usual expression of Clapeyron does hold.

A combination of the results of these last two paragraphs has immediate application to the experimental question mentioned in the introduction which started this inquiry. Suppose we have a liquid and solid in equilibrium, and we change the pressure supposedly equally on both phases by an increment dp of hydrostatic pressure, but that, because of imperfections in the apparatus, we actually apply an additional stress not hydrostatic to limited portions of the surface of the system. It is easy to see that melting or freezing takes place at the free surfaces with such changes of volume as to tend to produce throughout the mass just that change of hydrostatic pressure which we thought we had applied.

6. If instead of a liquid and a solid, we consider two solid phases, we see that the transition point may be either raised or lowered. If the normal stress across the surface of separation is unaltered by the applied stress system, then the transition point is always lowered when a stress system is applied exclusively to (2), and raised when applied to (1). The differentiation between (1) and (2) is provided by the sign of λ. There is, however, this difference between a liquid and a solid, and two solids. If the two solids are in equilibrium under hydrostatic pressure

and we try to increase pressure uniformly on both phases, but because of restraints in the apparatus actually apply it to only one of the phases, the reaction will in some cases *not* so run as to redistribute the pressure uniformly throughout the mass. That is, one phase may act as a protecting covering for another, so that the reaction need not run on passing the transition line, but will run at some remoter pressure, when the strength of the covering is exceeded. Such cases are not common, but do occur sometimes; ice V and VI afford an example.

7. Let us now consider the behavior of *crystalline* phases, either two polymorphic solids in contact, or a solid and liquid. We restrict ourselves to the cases usually met in practise where the phases are in elastic equilibrium at the surface of separation without the interposition of a permeable membrane; that is, we assume ${}_1N_\nu = {}_2N_\nu$. For those cases in which ${}_1N_\nu = -p$, the depression of the transition point is of the second order in the applied stress, and for those for which ${}_1N_\nu \neq -p$, the depression is of the first order. In both cases, the effect of the orientation and the specific crystalline constants on the depression is of a higher order. That is, the fact that the substance is crystalline enters the result only in so far as the surface stresses are determined by the orientation of the crystal. Given a crystal under a specified state of internal stress, and with specified stresses across the surface of separation from another phase, and the shift of the transition point is entirely determined by these elements alone (to quantities of the order concerned), and does not involve at all the orientation of the surface with respect to any of the elements of symmetry of the crystal. This result is evidently of importance as affecting the uniqueness of transition or melting points determined experimentally.

Application to Plasticity.

The fact that the melting point of a solid at a free surface is always depressed by any stress system whatever is suggestive and of considerable importance.[1] This fact offers the possibility of a theory of plasticity, in some respects similar to a previous theory, but free from some of its objections. This previous theory, suggested by Poynting,[2] and lately developed in much greater detail by Johnston,[3] depends on the fact that the melting point is always lowered by the application of hydrostatic pressure to the solid phase only, and lowered by an amount greatly exceeding the rise that would be produced by the same pressure applied hydrostatically to both phases. This formula was given above under

[1] This fact was stated by Gibbs.

[2] J. H. Poynting, Phil. Mag. (5), 12, 32, 1887.

[3] J. Johnston, Jour. Amer. Chem. Soc., 34, 788, 1912.

special case (2). For the purposes of this theory we consider that when a solid is stressed the pressure is taken up unequally by the miscroscopic crystalline grains, and that on some of these grains the pressure may be very intense. If it is so intense as to depress the melting point to the temperature of the surroundings, melting takes place at these grains, and we have flow of the metal as a whole, with the phenomena of plasticity.

The theory in this form seems to me to be open to several objections. It is most difficult to conceive how in any actual solid there is anything corresponding to the fictitious membrane which maintains the solid under hydrostatic pressure, while permitting the liquid to flow freely away. Certainly if in the solid there are any grains about which the surrounding material is not closely packed, the conditions of elastic equilibrium demand that at the surface at which the melting is to occur the normal stress be less than the average. In other words, no matter how intense the average pressure throughout any individual grain, at the free surface of this grain where the melting is to take place there can be no normal stress, and hence the conditions of the theorem do not apply. Another objection is that experimentally the plastic flow of a well-annealed metal begins at the same numerical value of the stress, whether in compression or tension. The fundamental formula gives a change of melting point directly proportional to the stress; under a tension the melting point is raised, and there should be no plastic flow at all. In other words, the theory accounts qualitatively for plasticity in compression but not in tension.

The theory modified as above is evidently not open to these objections. A solid subjected to any stress system whatever, either tension, compression, or shear, experiences a *depression* of the melting point at the *unstressed* surface (or at a surface stressed by less than the average amount) and melting will take place at that surface if the stress is high enough. This statement is free from all hypothesis as to the nature of the contact between the surfaces of the grains. The picture we form of a plastic flow is essentially the same as in the previous theory; that is, under some conditions flow is produced by an actual local melting, followed by regelation with equalization of pressure on all the grains. This local melting takes place when any grain is subjected to more than its share of the stress and so is subjected to a stress not hydrostatic.

It is now of interest to inquire of how wide application this contributory agent in plasticity is. Several reasons lead me to the opinion that it has not the universal importance that Johnston maintains in his theory, but that in most solids at points far below the melting point the more important part of the mechanism of plastic flow is of quite distinct origin.

One of these reasons is the effect of temperature on rate of flow. Tammann and his pupils[1] have found that the rate of flow under constant stress very nearly doubles for every 10° rise of temperature. This holds over considerable temperature ranges—to far below the melting point. If plasticity is really due to local melting, one would not expect so rapid a change, but would rather expect the rate to perhaps more nearly double when the distance to the melting point is approximately halved. Another reason is to be found in the values of the maximum stresses that solids will support without plastic yield. It is well known that the flow point may be raised by the previous application of stress. This is in all probability due to a readjustment of the crystalline grains so that the load is distributed more equally. On the above theory this readjustment is brought about by actual melting and regelation. But it is also well known that there is an upper limit beyond which the plastic limit cannot be raised. This upper limit is presumably reached when the readjustment between the grains has proceeded so far that each grain is uniformly stressed by its proper share. According to the theory under discussion, this upper limit should be reached at the theoretical stress, assumed uniformly distributed, requisite to depress the melting point to the prevalent temperature. As a matter of fact, the upper plastic limit is never so high. The following table shows the upper limit found experimentally by Tammann and Faust,[2] and the computed values taken from Johnston's paper. The table includes all the metals common to the two papers. The actual values are from 8 to 40 times too low, divergences so large as to belong to another order of magnitude. If Johnston's theory is correct, this would mean that after prolonged flow the internal readjustment of stress between the grains is still so imperfect that some grains always bear from 8 to 40 times their share of stress. If the maximum stress is computed by the newer formula suggested above, values are found which are of the order of 10 times greater again than Johnston's. The

Metal.	Flow Point.	
	Observed, Kgm./cm.²	Calculated, Kgm./cm.²
Pb	102	1,760
Sn	55	2,200
Cd	109	3,300
Al	600	5,100
Zn	770	6,900
Cu	2,780	24,000

[1] N. Werigin, J. Lewkojeff, and G. Tammann, Ann. Phys., 10, 647, 1902–03.

[2] O. Faust and G. Tammann, Zs. phys. Chem., 75, 108, 1910.

conclusion seems forced upon us that under ordinary conditions the mechanism of plasticity must be different from a partial melting. Pertiment suggestions as to what the mechanism may be are common in the literature.[1]

In some cases, however, plasticity by melting must be a real effect. Of course it must be of importance in the immediate neighborhood of the melting point. This means that no crystal continues rigid up close to the melting point, but softens in the immediate neighborhood. Experiments have been made on the plasticity of crystals near the melting point, and conclusions drawn as to the molecular mechanism. It is probable that a large part of this plasticity is due to minute traces of impurity just as is the increase of specific heat below the melting point. But quite apart from the effect of impurities, these considerations show that every crystal will be plastic near the melting point, independent of any special molecular mechanism, the plasticity being called into play by the very forces which must be applied to detect its existence. This kind of plasticity may also possibly enter at the very beginning of flow of a badly annealed piece of metal, in which the load is very unequally distributed among the grains.

Plasticity is to be expected not only near a melting point, but also near any polymorphic transition point, since any inequality of stress on the different grains produces a change of the transition point and consequently a reaction from one solid phase to another, accompanied by a change of volume and a readjustment that will show itself as flow. This plasticity will exist both above and below the transition point. In general, the range of plasticity about a transition point will be larger than about a melting point, because the heat of transition is usually less than the heat of melting. Because of the wide existence of polymorphism, this agent must be of geological importance.

To sum up these remarks on plasticity; under certain conditions plasticity is produced by an actual melting with regelation of those crystalline grains which bear the brunt of the stress. This local melting is governed by the equations for an unequally stressed solid, and not by the equations for a solid under hydrostatic pressure in equilibrium with a liquid not under pressure. This contribuory agent in plasticity does not seem, however, to be largely effective in the majority of the cases of practice. For some substances an analogous effect, due to displacement of polymorphic transition points, is of more importance.

THE JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.

[1] J. A. Ewing and W. Rosenhain, Phil. Trans. 193 (A), 353, 1900. J. C. W. Humfrey, Phil. Trans. 200 (A), 225, 1903, for example.

A NEW RELATION DERIVED FROM PLANCK'S LAW.

BY PAUL D. FOOTE.

OF the many possible relations which may be derived from the radiation law of Planck only a few have received any attention. The most important of these are the two displacement laws of Wien $\lambda_{max}\theta$ = constant and $J_{max}\theta^{-5}$ = constant. Salpeter[1] has defined a function of λ and θ as follows:

$$\eta(\lambda, \theta) = \frac{J_\lambda}{\int_0^\infty J_\lambda d\lambda}$$

where J_λ is the intensity of radiation of absolute temperature θ and wave-length λ as determined by Planck's law. The functions

$$\frac{\partial \eta}{\partial \lambda} = 0 \quad \text{and} \quad \frac{\partial \eta}{\partial \theta} = 0$$

have roots, the former expression giving $\lambda_m\theta$ = constant = 2,910 micron degrees for c_2 = 14,450 micron degrees, *i. e.*, identical with Wien's displacement law, and the latter expression $\lambda\theta_{max}$ = 3,686 micron degrees for the same value of c_2.

It is evident that any number of displacement laws may be derived from the Planck equation.[2] Thus $\lambda'\theta$ = constant where λ' may refer to any kind of corresponding points on the energy curves at various temperatures, for example, the point of inflection on each side of the maximum ordinate, etc. The present paper concerns the relation that the product of the absolute temperature and the λ-coordinate of the center of gravity of the spectral energy curve is a constant.

Let

(1) $$J_\lambda = c_1\lambda^{-5}(e^{c_2/\lambda\theta} - 1)^{-1} = \text{Planck's Law}$$

λ_c = the λ-coordinate of the center of gravity of the curve J versus λ. Then by the definition of center of gravity:

(2) $$\lambda_c = \frac{\int_0^\infty J_\lambda \lambda d\lambda}{\int_0^\infty J_\lambda d\lambda}$$

[1] Salpeter, Phys. Zeit., 15, 764–5, 1914.

[2] See Buckingham and Dellinger, Bureau of Standards, Scientific Paper No. 162, p. 405.

Put $x = c_2/\lambda\theta$. Equation (2) becomes:

$$\lambda_c = \frac{c_2}{\theta} \frac{\int_0^\infty x^2(e^x - 1)^{-1}dx}{\int_0^\infty x^3(e^x - 1)^{-1}dx}. \tag{3}$$

Expanding $(e^x - 1)^{-1}$ by division each term in both numerator and denominator takes the gamma function form and by the relation;

$$\int_0^\infty e^{-kx}x^{n-1}dx = \frac{\Gamma(n)}{k^n}$$

equation (3) may be expressed as follows:

$$\lambda_c = \frac{c_2}{\theta} \frac{\left(1 + \frac{1}{2^3} + \frac{1}{3^3} + \cdots\right)\Gamma(3)}{\left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \cdots\right)\Gamma(4)} \tag{4}$$

whence

$$\lambda_c = 0.37021\,\frac{c_2}{\theta}. \tag{5}$$

Equation (5) is the new relation derived from Planck's law. Thus for $c_2 = 14{,}450$, $\lambda_c\theta = 5{,}350$ micron deg.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

A STUDY OF RIPPLE WAVE MOTION.

BY F. R. WATSON AND W. A. SHEWHART.

WAVE motion has been made the object of a large number of theoretical and experimental investigations to determine the physical properties of waves and also to explain the various phenomena of reflection, refraction, diffraction and interference. One of the most satisfactory experimental methods of attack has been found in the study of ripple waves, since in this case, we can visualize almost every phenomena of wave motion.

The object of this paper is to describe the development of a method by which ripple waves may be generated not only in steady patterns but also in patterns in which the waves apparently move very slowly. This allows a leisurely examination of the various phenomena. The method also allows the convenient exhibition of the waves to a lecture audience.

Historically, the investigation of ripples began in 1871 when Lord Kelvin[1] observed that the propagation of ripples depended on surface tension. Matthieson[2] tested the validity of Kelvin's formula, but, because of the rough measurements of the waves set up by a pin point piercing a jet of water, failed to obtain a great degree of accuracy. Ahrendt,[3] Riess[4] and others made similar experiments, but it remained for Lord Rayleigh[5] to develop the first accurate method of investigation. To make visible the extremely small disturbances in the plane of the liquid surface, he used a modified form of Foucault's method of testing plane surfaces. Furthermore, he used the stroboscopic method for making the waves appear to stand still. Dorsey[6] and Watson[7] have extended and improved Rayleigh's method in making investigations on the surface tension of liquids.

Tyndall[8] first made use of ripple waves to illustrate wave motion. Later, Vincent[9] was able with more refined apparatus to obtain beautiful photographs of the same phenomena. H. Schultze[10] devised an electrical

[1] Phil. Mag. (4), Vol. 42, p. 375, 1871.
[2] Wied. Ann., Vol. 38, p. 118, 1889.
[3] Exner's Rep. der Physik, Vol. 24, p. 318, 1888.
[4] Exner's Rep. der Physik, Vol. 26, p. 102, 1890.
[5] Lord Rayleigh's Collected Works, Vol. III., p. 383.
[6] PHYS. REV., Vol. 5, p. 173, 1897.
[7] PHYS. REV., Vol. 12, p. 257, 1901.
[8] S. P. Thompson, "Light, Visible and Invisible," Chap. 1.
[9] Phil. Mag., Vol. 43, p. 417; 45, 191; 46, 290.
[10] Zeitsch. f. Instk., p. 151, 1907.

method for producing ripples, modifications of which have been made by Pfund[1] and Palmer.[2] Waetzmann[3] developed a method in which the waves were generated by intermittent puffs of air, and were made visible by flashes of light isoperiodic with the puffs. Waetzmann's method, with extensions and modifications, has been used in the present investigation.

Fig. 1 is a diagram of the apparatus. Ripple waves were generated by puffs of air blown against the water surface in the glass-bottomed tank *A*. The puffs were secured by cutting a tube conveying compressed air and inserting in the gap a disc with a circular row of equally spaced holes. When the disc rotated, the current of air was periodically interrupted. The waves were made visible by the stroboscopic method. Light from an arc lamp was focused on the row of holes in the rotating disc, thus giving flashes isoperiodic with the puffs of air. By reflecting the light upward through the glass tank, a steady pattern of waves was revealed. Fig. 2 shows a photograph obtained with circular waves.

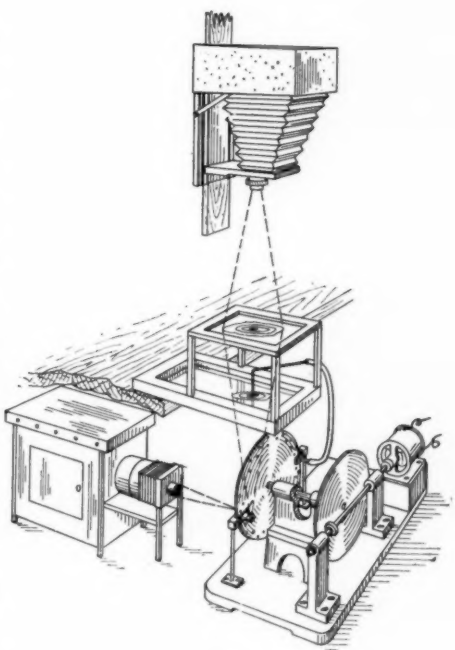


Fig. 1.

Diagram of apparatus showing how ripples are generated on a water surface by puff of air and made visible stroboscopically on the frosted glass plate above the water tank.

By using a second row of holes, which were fewer in number than those in the row already described, the flashes of light could be made to come a little slower than the puffs of air; the result being that the waves apparently moved forward slowly. This action allowed a leisurely study for the different phases of reflection, diffraction, etc., with slowly moving waves.

Trouble was experienced in getting steady patterns of waves, due to vibrations of the apparatus and fluctuations of the puffs of air. The vibrations were overcome by mounting the tank on a steady support. The fluctuations in the air puffs were almost entirely eliminated by using

[1] PHYS. REV., Vol. 32, p. 324, 1911.
[2] PHYS. REV., Vol. 33, p. 528, 1911.
[3] Physikalische Zeitschrift, Vol. 12, p. 866, 1911.

a cast iron disc 10 inches in diameter and one-fourth inch thick and facing it after it had been mounted on an axle so that it would run true. It was then mounted securely on a cast-iron base and rotated by a small wheel on an axle attached by a toggle joint to a 1/6-H.P. direct-current motor. Variation of the speed of the disc was obtained by changing the resistance in series with the motor and also by shifting the position of contact of the small wheel with the disc.

To make the flashes of light sharp and definite in position, an arrangement of two small screens, each pierced by a small hole, was placed over the edge of the disc so that light could pass only during the instant that a hole in the disc came into coincidence with the holes in the screens. The reflecting mirror, which was small in area, was made by polishing the end of a circular aluminum rod cut at an angle of 45° to its axis. The source of light was a carbon arc fed by a 110-volt direct current. It gave good illumination except for the colors explained by Mrs. Ayrton.[1] These proved to be troublesome when taking photographs. A pattern of waves that appeared well illuminated to the eye would show serious distortions on the photographic plate.

The position and form of the aperture for the puffs of air influenced the shape of the waves to a marked extent. Satisfactory results were obtained by using a small copper tube of about 1 mm. diameter placed near the water surface. It could easily be bent into any desired position.

The waves may be shown to an audience by mounting a mirror at an angle of 45° over the surface of the tank so that the light is reflected to a screen. For this purpose it is desirable to let more light through so that the pattern will be well illuminated. This makes the definition of the waves less sharp but still satisfactory enough for demonstration.

Figs. 2 to 7 show some of the patterns investigated. Fig. 4 shows a curious overlapping interference. The patterns in Figs. 5, 6, and 7 were obtained by placing metal forms on the bottom of the glass tank and allowing the water surface to barely cover them. The metal must be free from oil or grease. In Fig. 6 the diffraction waves were made more intense by shielding the central portion from the camera for part of the exposure. The time of exposure varied from 10 seconds to 20 minutes, depending on the amount of light. The length of the waves was measured to be nearly 0.4 cm.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS.

[1] "The Electric Arc," Chap. 1.

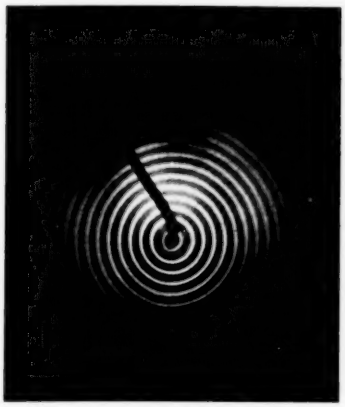


Fig. 2.
Circular waves.

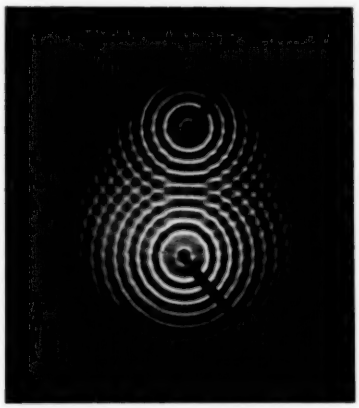


Fig. 3.
Interference of two sets of circular waves.

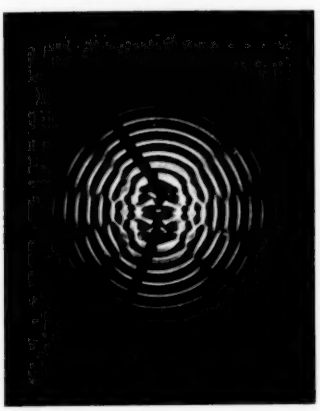


Fig. 4.
Interference of two sets of circular waves with sources close together.

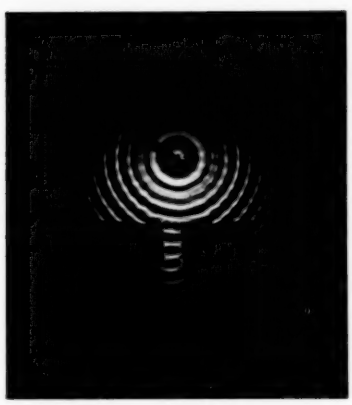


Fig. 5.
Diffraction through a narrow channel. Also reflection of waves.

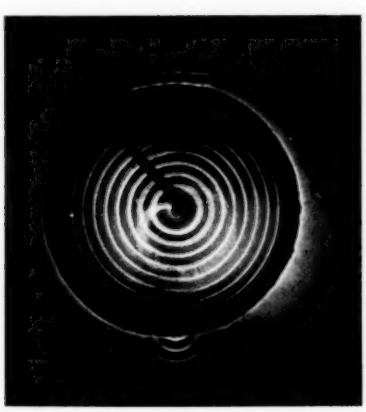


Fig. 6.
Diffraction of waves through narrow and wide aperture.

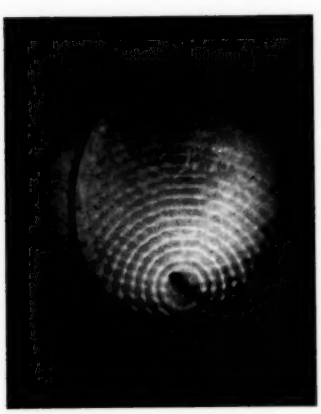


Fig. 7.
Reflection of waves in ellipse. Note the conjugate focus.

F. R. WATSON AND W. A. SHEWART.

THE DISTRIBUTION OF ENERGY IN THE NORMAL RADIATION SPECTRUM.

By Leigh Page.

IN their attempt to derive a radiation formula from classical dynamics Rayleigh and Jeans have been led to an expression which is in disagreement with experiment in so far as it demands that in the state of equilibrium the radiant energy in the ether should consist mainly of waves of infinitesimally short wave-length, and that the total energy per unit volume should be infinite. Lorentz has been led to the same expression by a consideration of the absorption and emission due to the free electrons contained in a piece of metal placed in a field of stationary radiation. In fact it has been asserted that this radiation formula is based only on the most general principles of classical dynamics and electrodynamics, and that any other expression for the distribution of energy in the normal radiation spectrum must be in contradiction to these principles.

The only radiation formula agreeing with experimental observation is that due to Planck. In obtaining his formula Planck considers the absorption and emission of ideal linear oscillators capable of executing only simple harmonic vibrations. His justification in using this special mechanism lies in the fact that Kirchhoff's law shows that the distribution of energy among the waves of different frequencies in a stationary field of radiation depends only upon the temperature of the material bodies with which the radiation is in equilibrium, and not at all upon their nature. However Planck finds it necessary, in order to obtain his formula, to make a number of revolutionary assumptions, at least one of which is in contradiction with classical electrodynamics. The following are the more important assumptions on which Planck bases his theory:

(*a*) While an oscillator absorbs energy continuously according to classical electromagnetic theory, the radiation of energy demanded by the electrodynamic equations is replaced by an emission by quanta. To be more specific, Planck assumes that an oscillator of frequency ν can emit only when its energy is an integral multiple of $h\nu$, h being Planck's constant, and that when emission does take place the oscillator loses all its energy and starts absorbing afresh. Such an assumption

not only involves a form of emission of energy utterly outside that contained in the electromagnetic theory, but is in contradiction with classical electrodynamics in that it supposes the radiation of energy demanded by the electrodynamic equations to be non-existent.

(*b*) The ratio of the probability of no emission, when the energy accumulated by an oscillator is an integral multiple of $h\nu$, to the probability of an emission is proportional to the intensity of the vibrations exciting the oscillator. If we grant assumption (*a*) assumption (*b*) seems reasonable, although its only justification lies in the fact that, in addition to the other assumptions, it enables Planck to deduce a formula which is in agreement with experimental facts.

(*c*) The constant of proportionality contained in assumption (*b*) is determined in such a way that the formula derived shall reduce to the Rayleigh-Jeans expression for long wave-lengths.

These three assumptions enable Planck to find the energy density of radiation for any frequency in terms of the average intrinsic energy of the oscillators of the same frequency with which the radiation is in equilibrium. To determine the value of the average energy of the oscillators in terms of their temperature, another assumption is necessary:

(*d*) If w is the probability that any given oscillator lies in any particular element of extension-in-phase, then in passing from one element of extension-in-phase to the next $\Delta w/w$ is not sufficiently small to make it possible to replace the summation by an integration in the expression for the entropy of the oscillators. In fact the elements of extension-in-phase are supposed to be of a size equal to the action quantum h. Consequently Planck finds for the average energy of a linear oscillator of frequency ν the expression

$$\frac{h\nu}{2} + \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

instead of the expression

$$kT \tag{2}$$

given by classical dynamics.

From these four assumptions Planck deduces the expression

$$u_\nu = \frac{\frac{8\pi h\nu^3}{c^3}}{e^{\frac{h\nu}{kT}} - 1} \tag{3}$$

for the energy density per unit frequency of homogeneous radiation of frequency ν and temperature T, c being the velocity of light in vacuum.

The object of this paper is to show that the radiation formula (3)

may be obtained from the expressions given by classical dynamics and electrodynamics for the absorption and radiation of energy, provided we make use of a single supplemental assumption in determining statistically the distribution of energy among the absorbing and emitting oscillators. We shall, like Planck, make use of Kirchhoff's law in that we shall consider a stationary field of radiation in equilibrium with ideal linear oscillators capable of executing simple harmonic vibrations. We shall imagine a large number of these oscillators of every frequency placed inside a rigid perfectly reflecting envelope, and allowed to come into equilibrium with one another and with the enclosed radiation. These oscillators will absorb and emit according to classical dynamics and electrodynamics. Hence if f is the electric moment of an oscillator in terms of Lorentz's unit of electric charge, the energy of its oscillatory motion at any instant will be given by

$$U = \tfrac{1}{2}L\dot{f}^2 + \tfrac{1}{2}Kf^2 = 2\pi^2\nu^2C^2L, \tag{4}$$

where L and K are constants, and where C is the maximum value of the electric moment, or the product of the amplitude of vibration by the charge. The rate of absorption of energy from the electromagnetic field will be given by[1]

$$\frac{dA}{dt} = \frac{u_\nu}{12L} \tag{5}$$

and the rate of radiation by[1]

$$\frac{dR}{dt} = \frac{2\pi\nu^2U}{3c^3L}. \tag{6}$$

So far we have made use only of classical dynamical and electrodynamical theory. To determine statistically the average value $\overline{U}$ of the energy of oscillations of frequency ν we shall now introduce a supplemental assumption, to wit:

The motion of an emitting and absorbing linear oscillator of frequency ν is stable only for those amplitudes for which the energy of its oscillations is an integral multiple of $h\nu$.

Hence the energy associated with an oscillation of frequency ν must be equal to $nh\nu$ where n is an integer. However it is not necessary for the development of our theory that the energy of the oscillation should be *exactly* $nh\nu$ but merely that it should lie between $nh\nu - \delta$ and $nh\nu + \delta$, where δ is very small compared to $h\nu$. Moreover it is not necessary to assume that the energy is, at every instant, an integral multiple of $h\nu$

[1] See "Planck's Heat Radiation" (translation by Masius) pages 160 and 165 for corresponding expressions in electrostatic units.

within the limits assigned above, but merely that the time during which the energy is *not* an integral multiple of $h\nu$ shall be very small compared to the time during which the energy is an integral multiple of $h\nu$.

In attempting to explain how this condition of the oscillator may be maintained—in view of the fact that the rate of absorption of energy is changing from instant to instant, and that even if the average absorption were just sufficient to balance the emission from an oscillator of energy $nh\nu$ it would not balance the emission from one of the energy $(n+1)h\nu$—it is necessary to remember that there are forms of restricted motion which involve neither emission nor absorption of energy. For example, a ring of evenly spaced electrons revolving in a circle about a positive charge placed at the center would neither emit nor absorb energy, so far as the motion in the plane of the circle is concerned. If such a ring, however, vibrated as a whole in a direction perpendicular to its plane, it would constitute one of the simplest types of linear oscillators consistent with Rutherford's model of the atom. So far as the degree of freedom involved in this vibration is concerned, there would be both absorption and emission of energy. However there might be some connection between the two degrees of freedom referred to, such that the energy associated with the absorbing and emitting degree of freedom might always tend toward an integral multiple of $h\nu$, any surplus or deficit of energy being taken care of by the other degree of freedom.

Again, there is no reason to suppose that an electron itself might not possess considerable energy of rotation. If the charge on the electron is distributed symmetrically with respect to its axis, there will be no emission of energy in consequence of its rotation. In addition to its rotation about a diameter, the electron might constitute the movable element of an ideal linear oscillator. Some connection between the vibratory motion and the rotation might result in a distribution of energy such that the energy of the oscillations would always tend toward an integral multiple of $h\nu$.

This speculation as to the method by which the vibratory energy of an oscillator is maintained at some integral multiple of $h\nu$ does not provide any mechanism by which the energy of the oscillations may pass from one integral multiple of $h\nu$ to another. Such a transition, however, would probably take place only during the encounters between different oscillators. In fact, if we are going to apply the theory of probability to the derivation of an expression for the average energy of an oscillator, we must suppose that such transfers of energy may occur. This does not limit the transfers of energy to cases where the ratio of the frequencies of the colliding oscillators has certain particular values. For if the

collision results in any surplus or deficit of oscillatory energy above or below the nearest integral multiple of $h\nu$, such surplus or deficit will be rapidly extinguished by transfer of energy between the emitting and non-emitting degrees of freedom.

A slightly different interpretation of our fundamental assumption would consist in the supposition that only when the energy of an oscillator was between $nh\nu - \delta$ and $nh\nu + \delta$ could the oscillator exist in the emitting and absorbing form. For energies outside of these limits the electrons and positive nuclei constituting the oscillator might form new aggregations such that their energy would be associated with types of motion involving no absorption or emission. A change of the energy content, as a result of collision, to the proper value would cause the elements of the oscillator to so rearrange themselves as to again constitute an absorbing and emitting mechanism. From this point of view we would have particles of all energies—the distribution of energy following the Maxwell-Boltzmann law—but only those whose energies were integral multiples of $h\nu$ would count in determining the conditions of equilibrium between matter and ether.

Average Energy of an Ideal Linear Oscillator in Terms of its Frequency and Temperature.

Suppose that we have inside a rigid adiabatic envelope N_1 linear oscillators of frequency ν_1, N_2 of frequency ν_2, etc. in thermal equilibrium with one another and with N_0 non-absorbing and non-emitting degrees of freedom. Since the energy of each oscillation is completely determined by its amplitude of vibration, the state of the system so far as the oscillations are concerned will be determined by the way in which N_1 oscillations of frequency ν_1, N_2 oscillations of frequency ν_2, etc., are distributed among the elements of extension-in-phase in a four-dimensional generalized space having as coördinates the three positional coördinates x, y, z, and q, where $q = C^2$. Since the energy of an oscillation of frequency ν is limited to values between $nh\nu - \delta$ and $nh\nu + \delta$, where n can assume integral values only, the elements of extension-in-phase will not fill the whole of this generalized space, and will have different positions for oscillations of different frequencies. For example, the projection on the x, y, q space of the elements of extension-in-phase for oscillations of frequency ν will be the solids bounded by the planes obtained by giving integral values to n in the equations

$$2\pi^2\nu^2qL = nh\nu - \delta,$$

$$2\pi^2\nu^2qL = nh\nu + \delta.$$

So far as the N_0 non-emitting degrees of freedom are concerned, the elements of extension-in-phase will fill the whole of the generalized space having as coördinates x, y, z and the variables determining the energy, since the energy associated with each of these degrees of freedom is in no way restricted to particular values.

Let us suppose that the state under consideration is one in which N_{00} non-emitting degrees of freedom are in element of extension-in-phase O_0, N_{01} in element of extension-in-phase I_0, etc., N_{10} oscillations of frequency ν_1 are in element of extension-in-phase O_1, N_{11} in element of extension-in-phase I_1, etc. Then the thermodynamic probability of the state, or the number of ways in which the state can be formed, is

$$W = \left\{ \frac{N_0!}{N_{00}!N_{01}!N_{02}!\cdots} \right\} \left\{ \frac{N_1!}{N_{10}!N_{11}!N_{12}!\cdots} \right\} \left\{ \frac{N_2!}{N_{20}!N_{21}!N_{22}!\cdots} \right\} \{\ \} \cdots,$$

where, of course, the second figure in the subscripts does *not* refer to the same element of extension-in-phase for oscillations of one frequency as for those of another, nor for oscillations as for non-emitting degrees of freedom, at least in so far as the coördinates specifying the energy are concerned.

Now the state of equilibrium is that state the probability of which is a maximum. Since the logarithm of a positive quantity is an increasing function of the quantity itself we may find the maximum of $\log W$ instead of that of W. If by w_{ij} we denote N_{ij}/N_i, *i. e.*, the mathematical probability of an oscillation of frequency ν_i being in element of extension-in-phase j, it may easily be shown that[1]

$$\log W = -\sum_i N_i \sum_j w_{ij} \log w_{ij}. \tag{7}$$

[1] In getting (7) from the expression for W use is generally made of Sterling's formula. A simpler and more direct method which obviates the use of Sterling's formula is the following:

If x is a large integer

$$\begin{aligned} \log x! &= \log 2 + \log 3 + \cdots + \log x \\ &\doteqdot \int_1^x \log x dx \\ &\doteqdot x \log x - x \end{aligned}$$

since the curve $y = \log x$ approaches parallelism to the x axis as x increases.

Hence

$$\begin{aligned} \log W &= \sum_i \{ \log N_i! - \sum_j \log N_{ij}! \} \\ &= \sum_i \{ N_i \log N_i - N_i - \sum_j N_{ij} \log N_{ij} + \sum_j N_{ij} \} \\ &= \sum_i N_i \{ \sum_j w_{ij} \log N_i - \sum_j w_{ij} \log N_{ij} \} \end{aligned}$$

as $\sum_j w_{ij} = 1$.

Hence

$$\log W = -\sum_i N_i \sum_j w_{ij} \log w_{ij}.$$

For equilibrium log W must be a maximum subject to the conditions that the total volume and the total energy remain constant.

For maximum of log W we have

$$\sum_i N_i \sum (\log w_{ij} + 1)\delta w_{ij} = 0.$$

From the constant volume condition we have as many equations as there are values of i, of the form

$$N_i \sum_j \delta w_{ij} = 0.$$

From the condition of constant total energy we get

$$\sum_i N_i \sum_j U_{ij}\delta w_{ij} = 0,$$

where U_{ij} is the average energy of a degree of freedom of type i in element of extension-in-phase j.

Using Lagrange's method of undetermined multipliers we get

$$w_{ij} = \alpha_i e^{-\beta U_{ij}}, \tag{8}$$

where β is independent of the type i of the particular degree of freedom under consideration while α_i is not.

So far as the non-emitting degrees of freedom are concerned U_{0j} may have any value from zero to infinity, although for oscillations of frequency ν_i, U_{ij} is limited to values between $nh\nu_i - \delta$ and $nh\nu_i + \delta$, except possibly for inappreciable periods of time immediately following collisions. Consequently expression (8) does not lead to the principle of equipartition of energy, namely that the average kinetic energy associated with each degree of freedom is $1/2\beta$ quite irrespective of its type or frequency. In fact, for the emitting and absorbing oscillations we have

$$w_{ij} = \alpha_i e^{-\beta nh\nu_i}. \tag{9}$$

Hence the average energy of an oscillation of frequency ν will be

$$\bar{U}_\nu = \frac{\sum_0^\infty N_\nu \alpha_\nu e^{-\beta nh\nu} nh\nu}{\sum_0^\infty N_\nu \alpha_\nu e^{-\beta nh\nu}}$$

$$= h\nu \frac{\sum_0^\infty n e^{-\beta nh\nu}}{\sum_0^\infty e^{-\beta nh\nu}}.$$

If we put $x = \beta h\nu$, we have

$$\overline{U}_\nu = h\nu \frac{e^{-x} + 2e^{-2x} + 3e^{-3x} + \cdots}{1 + e^{-x} + e^{-2x} + \cdots}$$

$$= h\nu \frac{e^{-x}}{(1 - e^{-x})^2}(1 - e^{-x})$$

$$= \frac{h\nu}{e^x - 1}. \tag{10}$$

In order to find x in terms of the temperature T we must first determine α_ν and β in terms of the total volume V and the total energy E_ν of all the oscillations of frequency ν. Let G_i denote the size of an element of extension-in-phase for oscillations of frequency ν_i. Then

$$G_i = \int\int\int\int dxdydzdq$$

$$= g_i \int\int\int dxdydz,$$

where $g_i = \int dq$.

Hence, for oscillations of frequency ν_i

$$\sum_j w_{ij} = \frac{\alpha_i g_i}{G_i} \sum_i e^{-\beta n h\nu_i} \int\int\int dxdydz$$

$$= \frac{Vg_i}{G_i} \frac{\alpha_i}{1 - e^{-x}}$$

since the elements of extension-in-phase fill up the whole of the x, y, z space, even though there are unoccupied gaps in the q space.

But

$$\sum_j w_{ij} = 1.$$

Therefore

$$\alpha_i = \frac{G_1}{Vg_i}(1 - e^{-x}). \tag{11}$$

If E_i is the total energy of all the oscillations of frequency ν_i

$$E_i = N_i h\nu_i \frac{\alpha_i g_i}{G_i} \sum_i n e^{-\beta n h\nu_i} \int\int\int dxdydz$$

$$= \frac{N_i h\nu_i}{e^x - 1} \tag{12}$$

as can be seen at once from (10).

Hence

$$e^x = 1 + \frac{N_i h\nu_i}{E_i}. \tag{13}$$

So, if we put

$$y = \frac{E_i}{N_i h\nu_i} = \frac{\overline{U}_i}{h\nu_i},$$

$$\beta = \frac{1}{h\nu_i} \log \left(1 + \frac{h\nu_i}{\overline{U}_i}\right) = \frac{1}{h\nu_i} \log \left(\frac{1+y}{y}\right) \tag{14}$$

and substituting the value of e^z from (13) in (11)

$$\alpha_i = \frac{G_i}{Vg_i} \frac{1}{\left(1 + \frac{\overline{U}_i}{h\nu_i}\right)} = \frac{G_i}{Vg_i} \frac{1}{(1+y)}. \tag{15}$$

Hence the probability w_{in} of an oscillation of frequency ν_i having an intrinsic energy between $nh\nu_i - \delta$ and $nh\nu_i + \delta$ is, from (9)

$$w_{in} = \frac{y^n}{(1+y)^{1+n}}. \tag{16}$$

Now we are ready to write down the expression for the entropy of the oscillations. If W_i is the thermodynamic probability of the state of equilibrium of the N_i oscillations of frequency ν_i, then the entropy S_i of these N_i oscillations will be, by definition,

$$S_i = k \log W_i. \tag{17}$$

As we are dealing with oscillations of a single frequency we can drop the subscript i. Hence

$$\begin{aligned} S &= k \log W \\ &= -kN \sum_j w_j \log w_j \\ &= -kN \left[\log \alpha - \frac{x}{e^x - 1}\right] \\ &= kN \log \left\{\frac{Vg}{G} \frac{(1+y)^{1+y}}{y^y}\right\}. \end{aligned} \tag{18}$$

Now, by definition

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_v.$$

Hence

$$\frac{1}{T} = \frac{k}{h\nu} \log \frac{1+y}{y},$$

$$\frac{1}{y} = e^{\frac{h\nu}{kT}} - 1 = \frac{Nh\nu}{E} = \frac{h\nu}{\overline{U}}$$

and

$$E = \frac{Nh\nu}{e^{\frac{h\nu}{kT}} - 1} \tag{19}$$

or[1]

$$\overline{U} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} . \tag{20}$$

Also

$$\beta = \frac{1}{h\nu} \log \frac{1 + y}{y} = \frac{1}{kT}, \tag{21}$$

which is independent of the frequency or nature of the oscillation, as it should be.

Moreover, we have from general thermodynamic theory

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_E$$

giving the laws of Charles, Boyle, and Avogadro, namely:

$$pV = NkT.$$

The Radiation Formula.

The radiation formula follows from the results of the preceding analysis at once. In the state of equilibrium the rate of radiation must, on the average, be equal to the rate of absorption. Hence from (5) and (6)

$$u_\nu = \frac{8\pi\nu^2 \overline{U}}{c^3} . \tag{22}$$

Substituting the value of $\overline{U}$ from (20) we get the radiation formula

$$u_\nu = \frac{\frac{8\pi h\nu^3}{c^3}}{e^{\frac{h\nu}{kT}} - 1} . \tag{23}$$

The Partition of Energy.

From the radiation formula we can find the way in which energy is distributed among the different degrees of freedom in the ether in the case of thermodynamic equilibrium. It is, however, necessary to emphasize one essential difference between the ether and material media.

[1] This expression is the same as that obtained from the first form of Planck's theory. Indeed much of our formal analysis is similar to that by means of which Planck first obtained his radiation formula, although the interpretation given is quite different. See Vorlesungen über die Theorie der Wärmestrahlung, first edition, page 157.

Energy travelling in the form of waves of frequency ν through a material medium may be converted in part or in whole into energy of another frequency by the agency of the medium itself. Such is never the case in the ether. Energy travelling through the ether in the form of waves of frequency ν will remain unchanged forever unless transformed into waves of another frequency by being absorbed and reemitted by matter. Hence the distribution of energy among the different degrees of freedom in the ether is conditioned entirely by the characteristics of the matter with which it is in equilibrium. Consequently this distribution would be quite different for ether in equilibrium with matter so constituted that the energy per degree of freedom associated with each radiating and absorbing oscillation of frequency ν is an integral multiple of $h\nu$, from what it would be if the material oscillations were capable of containing any amounts of energy whatsoever.

Consider N_1 linear oscillators of frequency ν_1, N_2 of frequency ν_2, etc., inside a rigid adiabatic perfectly reflecting envelope in thermal equilibrium with each other and with N_1' ethereal modes of vibration of frequency ν_1, N_2' ethereal modes of vibration of frequency ν_2, etc. The state of equilibrium is the one having maximum probability. Following the same line of reasoning as before, the probability that a material oscillation of frequency ν has an energy between $nh\nu - \delta$ and $nh\nu + \delta$ is, as before,

$$w = \alpha e^{-\beta nh\nu} \tag{24}$$

while the probability that any one degree of freedom of vibration in the ether of frequency ν has an energy U' is

$$w' = \alpha' e^{-\beta U'},$$

where U' is not restricted in value in the same way as is the energy of the material oscillations. Now the elements of extension-in-phase must be all of equal probability. Hence U', which denotes the *average* energy represented by an element of extension-in-phase, must change in going from one to the next by a constant amount, say ϵ. So we have

$$w' = \alpha' e^{-\beta n\epsilon}. \tag{25}$$

Consequently we can show by exactly the same method as used in the case of the linear oscillations in matter that the average energy $\overline{U'}$ associated with each degree of freedom in the ether of frequency ν is given by

$$\overline{U'} = \frac{\epsilon}{e^{\frac{\epsilon}{kT}} - 1}. \tag{26}$$

Now the number of degrees of freedom per unit volume of the ethereal modes of vibration of frequencies between ν and $\nu + d\nu$ is given by the well known expression

$$N d\nu = \frac{8\pi\nu^2 d\nu}{c^3}. \tag{27}$$

Consequently

$$u_\nu d\nu = \frac{\frac{8\pi\epsilon\nu^2}{c^3} d\nu}{e^{\frac{\epsilon}{kT}} - 1}$$

or

$$u_\nu = \frac{\frac{8\pi\epsilon\nu^2}{c^3}}{e^{\frac{\epsilon}{kT}} - 1}. \tag{28}$$

Comparing with (23) we see that

$$\epsilon = h\nu$$

and that *the average energy associated with each degree of freedom of a simple harmonic vibration of frequency ν, whether in matter or in ether, is given by*

$$\bar{U} = \bar{U}' = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}. \tag{29}$$

SUMMARY.

Planck's radiation formula has been derived from the expressions given by classical dynamics and electrodynamics for the absorption and radiation of energy with the aid of the supplemental assumption that the motion of an absorbing and emitting linear oscillator of frequency ν is stable only when the energy of its oscillations is an integral multiple of $h\nu$. This assumption avoids the necessity of replacing the emission of energy demanded by the electrodynamic equations by an emission that is discontinuous in time and difficult, if not impossible, to reconcile with the phenomena of diffraction and interference.

The partition of energy among the different degrees of freedom in the ether has been investigated, and found to be the same as in material oscillators.

SLOANE PHYSICS LABORATORY,
August, 1915.

CATHODE MEASUREMENTS WITH GLOW CURRENT IN HYDROGEN.

BY W. L. CHENEY.

PROFESSOR SKINNER[1] has recently developed a theory of the cathode fall in gases which suggests that with a plane cathode the "normal" current density should be proportional to the square of the gas pressure provided the number of mean free paths of the electrons from the cathode to the point of minimum gradient in the negative glow is the same for all pressures. In measurements made with aluminum and steel cathodes in hydrogen both of these conditions were found to exist.

He has also found that, provided the current density used is the same multiple of the "normal" current density, potential measurements in the region between the cathode and the negative glow, taken at various gas pressures and plotted against the number of mean free paths from the cathode, all lie on the same curve. For example, the potential difference obtained at "normal" current density at various gas pressures gave one curve, at twice "normal" current density a second curve, and so on.

The purpose of this research was to repeat some of Skinner's measurements with aluminum and steel and to extend the investigation to various other metals.

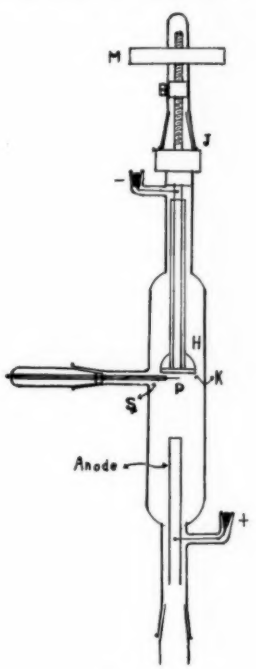


Fig. 1.

I. APPARATUS.

This consisted of a discharge tube (Fig. 1) about three centimeters in diameter, having a movable disc cathode K, carried by the micrometer screw B. The graduated drum M, on the ground joint J, served to give the axial position of the cathode. The current was confined to the front face of the cathode by the glass hood H. A probe wire P (Al, .24 mm. in diam.) sheathed to very near its end with a fine glass tube S, served to give the poten-

[1] C. A. Skinner, PHYS. REV., June and August, 1915.

tial in the gas. This sheath was renewed from time to time to prevent its becoming conductive as a result of metal sprayed off from the cathode.

Potential measurements were made by a quadrant electrometer in which a definite P.D. (6 volts) was placed between the quadrants, the potential sought being placed between one pair of quadrants and the needle. The electrometer was, from time to time, compared on a battery circuit with a Weston voltmeter. Customary precautions were taken against the possible influence of static charges and the more important leakage effects avoided by using sealing wax insulators throughout. This leakage was tested by placing a charge on the electrometer, disconnecting, and noting the rate at which the deflection changed. The change was not appreciable over a considerable length of time. In order to work rapidly—quite necessary in view of the deterioration of the gas—the deflections of the electrometer (read by telescope and scale) were taken only in one direction.

The current was furnished by a battery of small storage cells, giving in all about 1,100 volts; measured by means of a mil-ammeter or, for smaller currents, a d'Arsonval galvanometer; and regulated by means of a liquid rheostat consisting of a solution of cadmium iodide in amyl alcohol.

A description of the modified Dolazalek electrometer used may not be out of place. The regular needle of the electrometer was replaced by one of aluminum and the ordinary suspension by a ribbon of phosphor-bronze. A damping arrangement consisting of a fork of platinum, dipping into concentrated H_2SO_4, was used.

Another factor demanding care was the cathode surface. To insure uniform results, each day before beginning a series of observations (and often during the series) the cathode was freshly polished by scouring with Tripoli composite, by rubbing on a pad of felt, and finally by wiping carefully on a new piece of cheese cloth.

The hydrogen was obtained by the action of KOH on aluminum. Great care was exercised to rid the gas of air by initial pumping and flushing with hydrogen; also to thoroughly dry it by passing it, first through a tube containing P_2O_5, and then allowing it to stand for about a half hour in a chamber containing the same material. The hydrogen was then stored in a bulb (freed from occluded gases) connected with the apparatus, from which it could be drawn off as desired.

II. Experimental Results.

1. *Current Density and Number of Mean Free Paths to the Negative Glow with 'Normal' Cathode Fall.*—Cathodes of aluminum, steel, nickel,

zinc, and platinum were used. The gas pressures (measured by a McLeod gauge) were necessarily confined to the range of about one to four millimeters. With pressures below one millimeter the negative glow became crowded so closely to the cathode as to make distance measurements too uncertain. With each pressure the " normal " current density was obtained by increasing the current until the glow just covered the cathode and ceased to curl away from it, or (measuring with the electrometer) when the cathode fall began to rise. The former method was used in most cases, though at the very low pressures the latter was often resorted to. The point of minimum gradient was found, by moving the cathode toward the probe wire, and observing where the P.D. began to drop appreciably below the normal value given by the probe in the main part of the negative glow.

Before each set of observations, the cathode was cleaned by passing a heavy current through the tube; the gas then pumped out; and fresh gas introduced. With each gas filling the " normal " current, the " normal " cathode fall, and the distances to the point of minimum gradient were measured.

Representative results are given in Tables I.–V. The first column gives the pressures—each representing a fresh filling of gas. Column 2 gives the " normal " fall in volts; Column 3, the current density in milliamperes. Column 5 gives the mean free path (in mm.) of the electrons

TABLE I.

Aluminum Cathode in Hydrogen—Area = 3.0 sq. cm.

Gas Pressure (mm.).	Normal Fall (Volts.)	j_n (m.a.)	Dist. to Neg. Glow (mm.).	$\overline{\lambda}$ (mm.)	No. of m. f. p. to Neg. Glow.	$j_n \overline{\lambda}^2$
1.00	206	.067	10.80	.720	15.0	.0358
1.69	194	.193	6.60	.426	15.4	.0353
2.00	196	.287	5.33	.360	14.8	.0374
2.08	199	.307	5.36	.348	15.4	.0369
2.30	197	.400	4.82	.313	15.4	.0384
2.70	199	.550	3.99	.266	15.0	.0389
2.80	194	.607	3.98	.257	15.5	.0405
2.85	197	.613	3.98	.253	15.6	.0395
2.96	197	.683	3.72	.243	15.3	.0400
3.00	196	.653	3.75	.240	15.0	.0379
3.05	196	.713	3.66	.238	15.5	.0400
3.72	194	1.067	2.91	.194	15.0	.0400
3.90	196	1.167	2.78	.185	15.0	.0400
4.00	194	1.267	2.78	.180	15.4	.0410
Mean	197				15.3	.0387
Max. dev.	4.5%				3%	9%
Mean dev.	1%				1.5%	4%

TABLE II.

Steel Cathode in Hydrogen Area = 3.14 sq. cm.

Gas Pressure (mm. Hg.).	Normal Fall (Volts.)	j_n (m.a.).	Dist. to Neg. Glow (mm.).	$\bar{\lambda}$ (mm.).	No. m.f.p. to Neg. Glow.	$j_n\bar{\lambda}^2$
1.94	315	.191	7.70	.371	20.7	.0267
2.20	299	.270	6.70	.327	20.5	.0291
2.30	311	.245	6.42	.313	20.5	.0241
2.45	299	.314	5.88	.294	20.0	.0272
2.50	294	.350	5.76	.288	20.0	.0291
2.53	299	.350	5.70	.285	20.0	.0285
2.64	304	.334	5.70	.273	20.9	.0250
3.07	293	.540	4.70	.234	20.0	.0294
3.40	303	.620	4.24	.212	20.0	.0281
3.55	294	.700	4.15	.203	20.4	.0291
3.90	299	.780	3.85	.184	20.9	.0265
Mean	301				20.3	.0275
Max. dev.	4.5%				3%	12%
Mean dev.	2%				1.5%	5.5%

in hydrogen, at the corresponding gas pressure, as calculated from that of the molecule by using the ratio given by Franck and Hertz.[1] Column 6 gives the number of mean free paths to the minimum gradient, obtained by dividing the magnitudes in 4 by the corresponding ones in 5. Column 7, giving the product $j_n\bar{\lambda}^2$, is simply another way of expressing the relation

TABLE III.

Nickel Cathode in Hydrogen Area = 3.14 sq. cm.

Gas Pressure (mm. Hg).	Normal Fall (Volts).	j_n (m.a.).	Dist. to Neg. Glow (mm.).	$\bar{\lambda}$ (mm.).	No. of m.f.p. to Neg. Glow.	$j_n\bar{\lambda}^2$
1.72	325	.159	8.47	.419	20.2	.0281
2.50	328	.382	5.85	.288	20.3	.0317
2.81	319	.430	5.37	.256	21.0	.0283
2.90	322	.493	4.97	.248	20.0	.0307
3.06	323	.535	4.85	.235	20.6	.0296
3.54	316	.669	4.06	.203	20.0	.0278
3.60	325	.700	4.00	.200	20.0	.0281
3.73	320	.795	3.86	.193	20.0	.0296
3.80	324	.764	3.80	.190	20.0	.0275
4.03	320	.891	3.70	.178	20.8	.0286
Mean	322				20.3	.0290
Max. dev.	2%				3.5%	9%
Mean dev.	1%				1.5%	4%

[1] J. Franck and G. Hertz (Deutsch. Phys. Gesell., No. 9, p. 373, 1913) found the mean free path of the electron to be $4\sqrt{2}$ times the mean free path of the molecule. For 1 mm. pressure then the m.f.p. of the electron in hydrogen is about .72 mm.

TABLE IV.

Platinum Cathode in Hydrogen Area = 1.76 sq. cm.

Gas Pressure (mm. Hg.).	Normal Fall (Volts.)	j_n (m.a.)	Dist. to Neg. Glow (mm.).	$\bar{\lambda}$ (mm.).	No. of m. f. p. to Neg. Glow.	$j_n\bar{\lambda}^2$
1.61	310	.114	8.50	.446	19.0	.0231
1.95	306	.176	7.01	.369	19.0	.0239
2.21	302	.233	6.30	.326	19.3	.0249
2.35	300	.256	5.82	.306	19.0	.0240
3.05	303	.466	4.70	.236	19.9	.0260
3.10	303	.482	4.61	.232	19.9	.0260
3.35	300	.545	4.30	.215	20.0	.0252
3.60	299	.636	4.10	.200	20.5	.0254
3.86	297	.739	3.70	.186	19.9	.0257
4.00	304	.767	3.20	.180	20.0	.0249
4.34	302	.938	3.30	.166	19.9	.0260
Mean	302.5				19.7	.0250
Max. dev.	2.5%				3.5%	7%
Mean dev.	1%				2%	3%

j_n/p^2, since $\bar{\lambda}$ varies inversely as the pressure, p. Columns 2, 6, and 7 show for all metals merely irregular fluctuations about a certain mean value, thereby proving the constancy of the relations already stated.

Comparing the different metals, aluminum gives a much higher current density than the others, the lowest cathode fall, and the least number of

TABLE V.

Zinc Cathode in Hydrogen Area = 3.14 sq. cm.

Gas Pressure (mm. Hg.).	Normal Fall (Volts).	j_n (m.a.).	Dist. to Neg. Glow (mm.).	$\bar{\lambda}$ (mm.).	No. of m.f.p. to Neg. Glow.	$j_n\bar{\lambda}^2$
1.40	284	.108	9.25	.515	18.0	.0285
1.50	278	.130	9.15	.480	19.1	.0301
1.85	273	.203	7.35	.389	18.9	.0309
2.33	280	.302	5.85	.309	18.9	.0290
2.45	277	.346	5.30	.294	18.0	.0301
2.45	276	.344	5.30	.294	18.0	.0290
2.80	269	.460	4.85	.257	18.9	.0306
2.97	275	.509	4.36	.242	18.0	.0301
3.02	270	.557	4.40	.238	18.5	.0316
3.25	272	.620	3.99	.222	18.0	.0306
3.33	272	.685	4.00	.217	18.4	.0322
3.48	265	.764	3.81	.207	18.4	.0327
4.00	267	.923	3.24	.180	18.0	.0301
4.18	271	1.08	3.22	.172	18.7	.0322
Mean	273.5				18.4	.0306
Max. dev.	4%				4%	7%
Mean dev.	1.5%				2%	3%

mean free paths to the negative glow. The mean values of the cathode fall given here for aluminum and steel agree very closely with the values given by both Warburg[1] and Skinner.[2] The other results from these metals are also in excellent agreement with Skinner's as shown by the following table.

	Cheney.		Skinner.	
	Al.	Steel.	Al.	Steel.
Cathode fall (volts)	197	301	197	303.5
No. of m.f.p. from Cathode to minimum gradient.....	15.3	20.3	15.3	20.5
$j_n\bar{\lambda}^2$.....	.0387	.0275	.039	.0273

These comparisons, along with that of individual values given in the tables I–V., indicate that one is but slightly less certain of reproducing both $j_n\bar{\lambda}^2$ and the distance of the minimum gradient from the cathode than one is of reproducing the cathode fall itself.

Zinc ranges next to aluminum in the series of metals, having the next lowest cathode fall, the next highest current density, and the next smallest number of m.f.p.'s to the negative glow. Both zinc and nickel were rather difficult to work with, owing to tarnish. This necessitated frequent polishing of the cathode and many observations. The values given for these (tables III. and V.) are only those results which were obtained immediately after polishing and before any tarnish became apparent.

It is interesting to note that in the case of nickel, both the current density and the cathode fall are higher than in the case of steel, while the number of mean free paths from the cathode to the minimum gradient are the same.

With platinum much trouble arose from the distintegration of the cathode. In a relatively short time the metal would spray off so badly that it necessitated renewing the sheath and cleaning both the probe wire and the walls of the tube. With this metal, the cathode fall (302.5 volts) runs slightly higher than the value given by Warburg[1] (300 volts) and Capstick[2] (298 volts). The " normal " current density runs a trifle lower than for steel or nickel.

2. *Potential Curves in the Gas with ' Normal ' Current Density.*—Before each series of observations the cathode was cleaned as usual by a heavy

[1] E. Warburg, Wied. Annalen, 31, p. 542.
[2] C. A. Skinner, PHYS. REV., *l. c.*
[3] E. Warburg, Wied. Annalen, 31, p. 542.
[4] Capstick, Roy. Soc. Proc., 63, p. 356, 1898.

current, the tube evacuated, and fresh gas introduced. Starting at the negative glow, the P.D. between the cathode and points at various mean free paths from it (measured to the center of the probe) were obtained as rapidly as possible—the current being maintained at its normal value during the series of observations. Check values were always taken after each series to indicate if disturbing changes had arisen during the operation. Only those values are given where the change in the cathode fall during a series was less than 2.5 per cent.

The observations are incorporated in Tables VI. and VII. Table VI. gives the results in detail obtained from platinum. It shows that the magnitudes are practically the same at all gas pressures. In Table VII. are given therefore only the mean values obtained from Al 1, Al 2, Ni, steel, and Pt. These mean values were obtained in the same way as the values in Table VI.—Al 1 from 8 different gas pressures ranging from 1.7 to 5.0 mm.—Al 2 from 4 different pressures, from 1.1 up to 2.0 mm. only—steel from 11 different pressures, from 2.2 to 3.9 mm.—Ni from 8 different pressures from 1.7 to 4.0 mm.—and also Pt from those of Table VI.

TABLE VI.

Potential Curve—Platinum—"Normal" Current Density ($j_n\bar{\lambda}^2 = .0387$).

No. of m. f. p.	Gas Pressure in Mm.										Mean P. D.
	1.41	1.75	1.95	2.25	2.65	3.05	3.10	3.35	3.60	3.86	
3	175	178	175	170	173	174	176	—	—	173	174.5
4	—	190	190	182	185	189	191	183	183	187	187
5	200	202	204	193	196	200	203	198	197	201	199.5
6	—	—	215	204	207	214	215	210	208	213	211
7	222	224	228	215	218	227	228	222	219	224	223
9	245	244	248	237	238	246	249	241	237	244	243
13	274	278	281	265	274	276	269	270	265	269	272
17	293	293	301	290	286	294	295	289	290	288	292
20	302	302	306	299	294	303	303	300	299	297	301

Al 1 was the same cathode used in previous measurements. Comparing these results with those obtained by Skinner, the P.D. between the cathode and two mean free paths from it differed by about 7 per cent. To ascertain if this were due to a difference in the samples of the metal his cathode (Al 2) was also tried. The results are practically the same as given by Al 1 at the same gas pressure. The discrepancy in our results is somewhat larger than the conditions would ordinarily allow.

Skinner calls attention to the divergence of the potential curves at low gas pressures from the constant relation illustrated in Table VI. the difference shown here between Al 1 and Al 2 arises from this fact—the

observations for Al 1 being simply those obtained below 2 mm., while for Al 2 they range from 1.7 up to 5 mm.

Observations were also made with zinc but the results were very inconsistent, indicating conductivity of the probe sheath.

TABLE VII.

Potential Curves "Normal" Current Density.

Number m.f.p. from Cathode.	Mean P.D.'s				
	Al 1.	Al 2.	Steel.	Nickel.	Platinum.
2	107	100	171	——	——
3	119.5	124	187	213	174.5
4	131	137	198	225	187
5	142	152	208	237.5	199.5
6	154	164	218	248	211
7	163	172	227	257	223
9	179	186	243	274	243
11	190	194	——	——	——
12	——	——	267	291	——
13	193	——	——	——	272
15	196	197	——	——	——
16	——	——	285.5	309	——
17	——	——	——	——	292
20	——	——	——	320	301
20.5	——	——	297	——	——

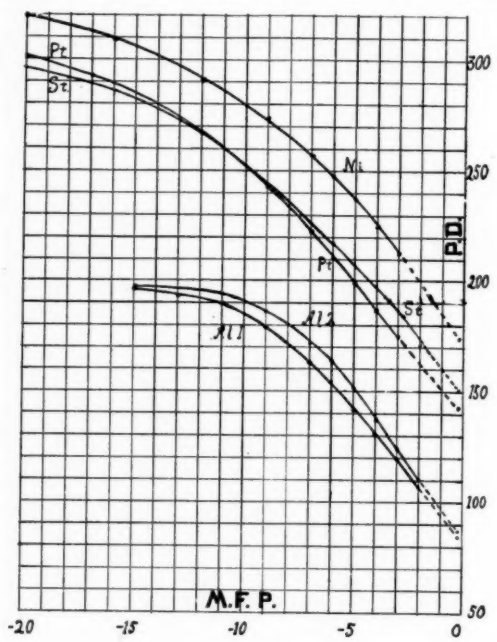


Fig. 2.

The results of the observations in Table VII. are plotted as curves in Fig. 2 with mean free paths as abscissæ and P.D.'s as ordinates. The broken line parts of these curves (practically straight) are their theoretical extension up to one m.f.p. of the positive ion from the cathode —over which the fall of potential between the cathode and the gas is conceived to occur. The method of obtaining these theoretical values follows later. A comparison of these values with the total cathode fall in the gas is given in the following table (VIII.):

TABLE VIII.

Cathode.	Total Cathode Fall (Volts).	Fall in Gas.	Fall at Cathode.
Al 1	196	111.5	84.5
Al 2	197	110	87
Steel	297	146	151
Nickel	320	145.5	174.5
Platinum	301	158	143

It is interesting to note that with Al and Pt the larger part of the fall is in the gas while with the other metals the larger part is between the cathode and gas.

III. SOME APPLICATIONS OF THE RESULTS.

1. *Mobility of the Positive Ions.*—This is defined as their velocity in cm. per sec. in unit field. From the potential measurements given in Table VII., the upper and lower limits of the mobility of the positive ions can be calculated from expressions given by Skinner (*l. c.*). These are

$$\begin{aligned} V_0 - V_1 &< \left\{ \left(\frac{16\pi j}{9\dot{\mu}} \right)^{\frac{1}{3}} (x_1 - x_0) \right\}^{\frac{3}{2}} \\ &> \left\{ \left(\frac{16\pi j}{9\dot{\mu}} \right)^{\frac{2}{3}} (x_1 - x_0) - \epsilon^{\frac{2}{3}} \right\}^{\frac{3}{2}} + \epsilon \end{aligned} \tag{1}$$

in which $V_0 - V_1$ is the difference of potential (in electrostatic units) between some point x_1 near the cathode and x_0 the point of minimum gradient; j is the current density in electrostatic units; $\dot{\mu}$ is the mobility of the positive ions also in electrostatic units; and ϵ is the ionizing potential of the electron[1] (11 volts or .037 electrostatic unit).

From these expressions it follows that

$$\begin{aligned} \dot{\mu} &< \frac{16\pi}{9} j \frac{(x_1 - x_0)^3}{(V_0 - V_1)^2} \\ &> \frac{16\pi}{9} \frac{j(x_1 - x_0)^3}{\{(V_0 - V_1 - \epsilon)^{\frac{2}{3}} + \epsilon^{\frac{2}{3}}\}^3} \end{aligned} \tag{2}$$

[1] J. Franck and G. Hertz, Deutsch. Phys. Gesell. Verh., 15, 2, p. 34, 1913.

To get the mobility in a field of one volt per cm. the values of $\overset{+}{\mu}$ given by (2) must be divided by 300.

Substituting from Table VII.—x_1 being taken as the point where measurements were made nearest the cathode and $(x_1 - x_0)$ obtained by multiplying the distance in m.f.p. by .072 cm. (the m.f.p. of the electron at 1 mm. pressure)—the limits of $\overset{+}{\mu}$ for a gas pressure of 1 mm. were calculated. These are given in Table IX. The values found here for the two samples of aluminum (2.3×10^4 and 3.7×10^4 cm./volt) agree closely with Skinner's values (2.2×10^4 and 3.6×10^4). There is also good agreement for Al, steel and Ni, while Pt gives a distinctly lower mobility—probably the effect of the presence of the metallic vapor arising from the disintegration of the cathode, the vapor hindering the progress of the positive ions toward the cathode.

TABLE IX.

Mobility of Positive Ions at One mm. Pressure.

Metal.	Lower Limit of $\overset{+}{\mu}$.		Upper Limit of $\overset{+}{\mu}$.	
	Electrostatic.	cm./volt.	Electrostatic.	cm./volt.
Al 1	$7.0\times10^6\frac{\text{cm.}}{\text{sec.}}$	$2.3\times10^4\frac{\text{cm.}}{\text{sec.}}$	$11.0\times10^6\frac{\text{cm.}}{\text{sec.}}$	$3.7\times10^4\frac{\text{cm.}}{\text{sec.}}$
Al 2	7.0×10^6	2.3×10^4	11.0×10^6	3.7×10^4
Steel	8.0×10^6	2.7×10^4	11.8×10^6	3.9×10^4
Nickel	7.0×10^6	2.3×10^4	10.5×10^6	3.5×10^4
Platinum	5.6×10^6	1.9×10^4	8.4×10^6	2.8×10^4

2. *Fall at the Cathode.*—By using the above values of $\overset{+}{\mu}$ in their respective expressions in (1) the potential curves may be extended to the cathode, or better to one mean free path of the positive ion from the cathode—this being considered as the region within which the positive ions causing the immediate fall between the gas and the cathode accumulate.

These calculations give the following values for the fall between the cathode and the adjacent gas. It appears surprising that the upper and lower limits of $\overset{+}{\mu}$ give so nearly the same values.

TABLE X.

Metal.	Fall at One m. f. p. of Positive Ion from the Cathode.		
	Upper Limit.	Lower Limit.	Mean.
Al 1	85	84	84.5
Al 2	88	86	87
Pt	143	143	143
Steel	152	150	151
Nickel	177	172	174.5

3. *The Magnitude of the Electron Current from the Cathode.*—Assuming that each electron leaving the cathode results in two electrons at one m.f.p., four at two m.f.p., and so on; and, that in the region of lower gradient the number of electrons doubles in moving through the ionizing potential, Skinner calculates that the ratio of the electron current density ($\bar{j}_k$) from the cathode to the total current (j) is

$$\frac{\bar{j}_k}{j} = \frac{\bar{\mu}}{\bar{\mu} + \dot{\mu}} \cdot 2^{-\left\{\frac{x_k - x_a}{\lambda} + \frac{V_0 - V_a}{\epsilon}\right\}} \qquad (3)$$

where $[(x_k - x_a/\lambda)]$ is the number of mean free paths between the cathode and the point where ionization ceases to take place at every mean free path, $V_0 - V_a$ the fall of potential between this point and the negative glow, ϵ the ionizing potential, and $\bar{\mu}$ and $\dot{\mu}$ the mobilities in the low gradient region of the negative glow. Assuming that $\bar{\mu}$ and $\dot{\mu}$ are practically equal the following values for $\bar{j}_k/j$ were obtained.

TABLE XIV.

Metal.	$\frac{x_k - x_a}{\lambda}$	$\frac{V_0 - V_a}{\epsilon}$	$\frac{\bar{j}_k}{j}$
Al 1	6	3.8	57×10^{-5}
Al 2	6	3.0	98×10^{-5}
Ni	6	6.5	8.4×10^{-5}
Steel	6	7.2	5.3×10^{-5}
Pt	7	7.1	2.8×10^{-5}

Al 2 gives nearly twice the electron current of Al 1 (which is somewhat larger than the value obtained by Skinner). The effect of this is shown in the potential curve (Fig. 2)—Al 2 reaching a constant value at a somewhat shorter distance from the cathode. The difference does not arise from a difference in the samples of the metal but merely shows the effect of lowering the gas pressure, as already noted. The ratio $\bar{j}_k/j$, although very small for all metals, is about 7 times as large with Al 1 as with Ni, 10 times as large as with steel, and about 19 times as large as with Pt.

It is also interesting to note that with all metals, the point at which ionization at every collision takes place extends to about 6 m.f.p. from the cathode.

SUMMARY.

1. The " normal " current density at the cathode has been measured in hydrogen with Al, steel, Ni, Zn, and Pt as cathodes, and found in all cases to be proportional to the square of the gas pressure.

2. The number of mean free paths of the electron from the cathode to the point of minimum gradient in the negative glow has been measured for these metals under the same conditions and found to be independent of the gas pressure.

3. Potential curves in the gas between the cathode and the negative glow have been obtained at "normal" current density with these metals as cathodes. The potentials plotted against the number of mean free paths of the electron from the cathode lie, for all pressures, practically on the same curve.

4. From these potential measurements, the mobility of the positive ions has been calculated and consistent values obtained for all metals except platinum where the mobility is somewhat low, probably arising from the presence of metal vapor.

5. The potential curves have been theoretically extended to the cathode, and the fall between the cathode and the gas obtained therefrom.

6. The ratio of the electron current from the cathode to the total current has been calculated for the various metals.

I wish to express my sincere thanks to Professor C. A. Skinner for suggesting this problem and directing its course, also to Dr. A. Q. Tool for many helpful suggestions.

BRACE LABORATORY OF PHYSICS,
UNIVERSITY OF NEBRASKA,
June, 1915.

CATHODE MEASUREMENTS WITH GLOW CURRENT IN OXYGEN AND NITROGEN.

BY W. NEUSWANGER.

IN a recent paper, Prof. Skinner[1] has developed a theory of the so-called cathode fall in gases which gives a general relation between the fall, the current density, the mean free path of the electron, and the distance from the cathode to the point of minimum potential gradient in the negative glow. A series of experimental results with hydrogen substantially corroborated the theoretical deductions. The purpose of this investigation has been to make a similar experimental study of the cathode fall in oxygen and nitrogen.

APPARATUS.

The apparatus consisted essentially of a discharge tube, Fig. 1, connected with a McLeod gauge, a gas generator and storage chamber, and a mercury vacuum pump. The tube, which was similar to the one used by Skinner, was provided with a circular disk cathode K, carried on a threaded shaft S, whereby it could be accurately adjusted, through the ground joint J, to any given distance from the aluminum probe wire P, which served to give the potentials in the gas. The distances were indicated by the graduated drum D. To insure a fixed position of the nut N, the air pressure forced J against a shoulder Q, cemented on the stem of the tube. A glass hood H confined the discharge to the front face of the cathode. The diameter of the probe wire (.125 mm.) was about one half that used by Skinner (.24 mm.) in hydrogen—making it about the same relative to the magnitude of the mean free paths of the electrons in oxygen and nitrogen, as his was to that in hydrogen. This probe was covered by a close fitting glass sheath which was frequently renewed since any metallic deposit would render it conductive and hence give spurious potentials.

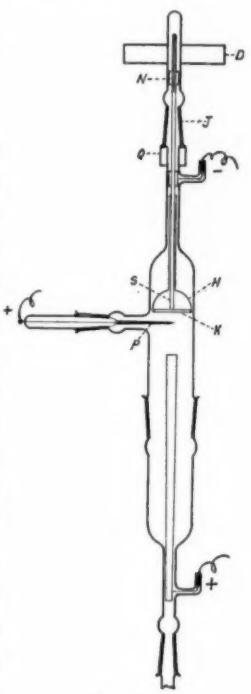


Fig. 1.

[1] C. A. Skinner, PHYS. REV., June and August, 1915.

The electrometer used was a modified Dolazalek fitted with a phosphor-bronze suspension and an aluminum needle. A constant potential difference of 18 volts was placed between the two pairs of quadrants, while that to be measured was placed between the needle and one pair of quadrants. The electrometer was calibrated from time to time by comparison (on a storage battery circuit) with a Weston voltmeter. In order to avoid leakage, the electrometer itself, together with the batteries used to charge the quadrants, were placed on sealing wax—no ground to the electrometer being used. All connecting lines and switches were similarly insulated. The electric current was furnished by a 1,200-volt battery of accumulators and regulated by a liquid resistance of amyl alcohol and cadmium iodide. It was measured by a Weston milliammeter.

EXPERIMENTAL.

Oxygen.

Oxygen was generated by heating a mixture of potassium dichromate and concentrated sulphuric acid. The gas was allowed to stand for several hours in a bulb containing crushed potassium hydrate to remove any acid vapor, and then after being thoroughly dried over phosphorous pentoxide, was stored in a chamber connected to the discharge tube, to be drawn off as desired.

Current Density and Number of Mean Free Paths to the Negative Glow with Normal Cathode Fall.—The general plan followed was to clean and polish the cathode, mount it in the discharge tube, evacuate this and flush with the gas. With the gas reasonably pure, an electric current was then passed through the tube which always increased the pressure by freeing occluded gases from the cathode. This impure gas was then removed and fresh introduced in which the measurements were made, namely: of the gas pressure, the normal cathode fall, normal current density, and the number of mean free paths of the electron from the cathode to the point of zero gradient. This set was then followed by a similar one in fresh gas—the process being repeated until the normal cathode fall rose above what was considered a satisfactory magnitude. The cathode was then removed and again carefully polished with Tripoli composite, and a new clean piece of cheese cloth before further measurements were made.

Series of observations with each of the metals, aluminum, steel, and zinc as cathodes, are given in Tables I., II. and III. respectively. Each gas pressure, column 1 of each table, represents a new gas filling. At pressures below those given, the luminosity was too faint to allow accur-

ate adjustment to normal current density. At higher pressures than those given, the other magnitudes became inaccurate. In column 2 is given the

TABLE I.

Aluminum Cathode in Oxygen. Area of Cathode: 1.35 sq. cm.

Gas Pressure (mm.).	Normal Cathode Fall (Volts).	Normal Current Density (j_n)	Distance to Neg. Glow ($x_k - x_0$).	Mean Free Path ($\bar{\lambda}$)	($j_n \bar{\lambda}^2$)	$\left(\frac{x_k - x_0}{\bar{\lambda}}\right)$
1.06	301	.44 ma.	4.20 mm.	.41 mm.	.074	10.2
1.45	306	1.04	3.30	.30	.090	11.0
1.58	312	1.33	2.50	.28	——	——
1.80	313	1.63	2.50	.24	.092	10.4
1.80	307	1.56	2.60	.24	.092	10.8
1.98	312	1.85	2.30	.22	.087	10.4
2.27	308	2.15	2.10	.19	.076	11.0
2.35	312	2.52	1.90	.19	.090	10.0
2.85	309	3.34	1.60	.15	.074	10.7
2.88	313	3.48	1.65	.15	.079	10.7
3.27	311	4.52	1.50	.13	.076	11.5
3.51	316	5.18	1.25	.125	.081	9.6
3.71	312	5.33	1.30	.12	.076	10.8
3.87	312	5.77	1.30	.11	.070	——
3.93	317	7.18	1.15	.11	.087	10.4
4.16	316	6.81	1.20	.105	.075	11.4
Mean	311			Mean	.081	10.6
Max. dev.	3%			Max. dev.	12%	10%
Mean dev.	1%			Mean dev.	8%	4%

normal cathode fall with its percentage deviation, in all cases surprisingly small. Column 3 gives the normal current density. This was found to decrease rather rapidly below that required to cover the cathode when first starting the current. However, consistent values could be obtained if the time interval required to make the reading was consistent. The method used here was to take the mean of the first two adjustments to the point at which the cathode glow just covered the surface of the electrode with uniform brightness. These were of course made as quickly as careful judgment would allow. The high value of the normal current density in oxygen as compared with hydrogen—six times as large as the same gas pressure—made it advisable to use cathodes of about 1.3 sq. cm. area instead of 3.0 sq. cm., as used by Skinner for hydrogen. The distance, in millimeters, from the cathode to the point of minimum potential gradient, given in column 4, was observed by noting where the potential began to decrease as the cathode was moved toward the probe wire, or, as described by Skinner, by setting the probe wire just in the outer face of the bright striation next to the cathode dark space. The

values of the mean free paths of the electron, column 5, corresponding to the given pressure were obtained from the relation given by J. Franck and G. Hertz,[1] namely: $4\sqrt{2}$ times the mean free path of the molecule. Column 7 obtained by dividing the distances in column 4 by the corresponding $\bar{\lambda}$ gives the number of mean free paths from the cathode to the negative glow. This according to theory should be a constant under conditions giving a constant cathode fall. Column 6 is the product of the normal current density by the square of the mean free path of the electron.

TABLE II.

Steel Cathode in Oxygen. Area of Cathode: 1.36 sq. cm.

Gas Pressure (mm.).	Normal Cathode Fall (Volts).	Normal Current Density. j_n	Distance to Neg. Glow. $x_k - x_0$	Mean Free Path. $\bar{\lambda}$	$j_n\bar{\lambda}^2$	$\frac{x_k - x_0}{\bar{\lambda}}$
1.05	336	.38 ma.	4.30 mm.	.42 mm.	——	10.2
1.37	338	.59	3.70	.32	.060	11.5
1.55	340	.77	3.30	.28	.060	11.8
1.65	343	.81	——	.27	.059	——
1.83	340	1.07	2.80	.24	.063	11.7
2.23	342	1.54	2.20	.20	.060	11.0
2.27	341	1.62	1.91	.19	.058	10.0
2.62	344	2.06	1.77	.17	.061	10.6
2.67	342	2.20	1.72	.16	.056	10.6
2.80	341	2.42	1.65	.16	.061	10.3
3.02	343	2.86	1.50	.145	.061	10.3
3.03	342	2.79	1.56	.14	.055	11.4
3.21	343	3.02	1.52	.14	.059	10.7
3.23	344	3.09	1.47	.135	.057	11.1
3.37	345	3.31	1.52	.13	.056	11.5
3.58	345	3.53	1.37	.12	.050	11.7
3.81	346	3.75	——	.115	.049	——
3.83	345	4.11	1.26	.115	.054	11.3
3.96	344	4.11	1.30	.11	.050	11.8
4.08	344	4.41	1.22	.11	.053	10.9
4.14	346	4.71	1.19	.105	.052	11.4
4.25	347	4.64	1.17	.10	——	——
Mean	343			Mean	.057	11.0
Max. dev.	2%			Max. dev.	13%	10%
Mean dev.	1%			Mean dev.	5%	4%

This too should be constant. Inspection shows for all three metals that throughout the range of gas pressures used, the normal cathode fall, and the number of mean free paths of the electron to the point of minimum potential gradient, are all practically constant. In the case of aluminum, several different samples of metals were used, all giving similar results.

[1] J. Franck and G. Hertz, Ber. d. Deutsch. Phys. Ges., 9, 1913, p. 373.

Comparing the different metals we find aluminum to give, as expected, the lowest cathode fall, 311 volts; next is steel with 343 volts; and then zinc with 354 volts. These values are from two to three per cent. higher than those found by Skinner.[1] The values of the other constants show a

TABLE III.

Zinc Cathode in Oxygen. Area of Cathode: 1.34 sq. cm.

Gas Pressure (mm.).	Normal Cathode Fall, (Volts).	Normal Current Density, j_n.	Distance to Neg. Glow, $x_k - x_0$.	Mean Free Path, λ.	$j_n\bar{\lambda}^2$	$\frac{x_k - x_0}{\bar{\lambda}}$
1.31	353	.46 ma.	3.90 mm.	.33 mm.	.050	11.8
1.45	354	.67	3.14	.30	.060	10.3
1.57	353	.66	——	.28	.052	——
2.13	356	1.19	——	.21	.053	——
2.35	354	1.49	2.31	.19	.054	12.1
2.38	354	1.64	2.05	.18	.052	11.7
2.42	354	1.64	2.19	.18	.052	12.2
2.63	354	1.94	1.96	.17	.055	11.7
2.73	354	2.16	1.75	.16	.056	10.6
2.94	354	2.62	1.66	.15	.058	11.3
3.13	355	2.80	1.54	.14	.055	10.7
3.32	355	3.54	1.38	.13	.059	10.8
3.60	354	4.11	1.32	.12	.059	10.8
3.62	356	3.96	1.33	.12	.056	10.8
3.79	356	4.63	1.38	.115	.061	12.2
3.91	356	4.40	1.34	.11	.053	11.8
3.96	355	4.77	1.20	.11	.058	10.9
4.24	352	5.15	1.18	.10	.052	12.0
4.28	355	5.22	1.22	.10	.052	12.0
4.46	352	6.05	1.11	.10	.058	11.2
4.52	356	5.90	——	.095	.055	——
4.78	354	6.71	1.04	.090	.056	10.9
Mean	354			Mean	.055	11.4
Max. dev.	.6%			Max. dev.	11%	11%
Mean dev.	.3%			Mean dev.	5%	5%

considerably larger variation than the cathode fall, as might be expected when the accuracy of the settings made for these is considered. The values of $j_n\bar{\lambda}^2$ for aluminum and steel are in about the same ratio, 3:2, as found by Skinner for hydrogen—both being about twice as large in oxygen as in hydrogen. Zinc gives about the same value as steel. As with the cathode fall the number of mean free paths to the negative glow differs but little with the different metals. As should be expected, also, the metals are in the same sequence here as with the cathode fall, the metal having the highest fall giving the greatest distance to the negative glow. These results show that the same general relation holds with oxygen as

[1] C. A. Skinner, Phil. Mag., 6, VIII., p. 387.

found by Skinner with hydrogen, namely:—*all gas pressures giving the normal cathode fall have the same number of mean free paths to the point of minimum potential gradient in the negative glow, and, have a normal current density proportional to the square of the gas pressure, i. e., inversely proportional to the square of the mean free path of the electron.*

Potential Curves in the Region between the Cathode and the Negative Glow.—Skinner found with hydrogen that the difference of potential between the cathode and any point at the same number of mean free paths from it is practically the same at various gas pressures, if the current density is the same multiple of the normal current density. The following gives the results of a similar investigation for oxygen.

For obtaining these potential curves an aluminum cathode was used with normal, twice normal and four-normal current densities. The same precautions were observed here as in the other tests, the probe sheath being renewed more often, since any leakage with it in the less conductive space near the cathode would cause greater error than with it in the highly conductive negative glow.

TABLE IV.

Potential Difference in Volts between the Cathode and Points in the Gas at a given Number of Mean Free Paths from it. Aluminum Cathode in Oxygen. For Normal Current Density: $j\tilde{\lambda}^2 = .081$

Gas Pressure (mm.).	Number of Mean Free Paths.						
	2	3	5	7	9	10	11
1.34	198	230	272	300	310	312	312
1.39	205	236	278	305	312	312	313
1.49	194	225	272	300	310	312	313
1.56	205	238	279	301	306	306	306
1.92	211	246	290	311	315	315	314
2.02	210	245	292	312	316	316	316
2.04	205	231	268	296	307	308	308
2.24	211	243	283	306	315	318	318
2.27	210	238	270	304	309	312	313
2.28	228	253	282	302	312	313	313
2.45	220	248	282	302	314	315	315
2.50	213	242	282	302	307	307	307
2.54	220	250	282	302	312	314	314
2.64	203	232	272	292	311	313	313
2.67	226	250	278	298	311	313	313
2.72	216	249	282	301	306	306	306
2.82	222	254	286	306	314	315	315
3.04	223	256	287	306	314	316	316
3.08	236	264	290	308	312	312	312
3.08	223	254	287	306	313	315	315
Means:	214	244	281	303	311	312	312

The procedure was to start with a fresh gas filling, and with the probe first in the negative glow, then at positions successively nearer the cathode, the difference of potential between it and the cathode was observed—all with a constant current maintained through the gas. These observations were taken as rapidly as possible to reduce the magnitude of the time changes—indicated by repeating the first observation at the close of each series. In the results given—incorporated in Tables IV., V. and VI.—the time change in the cathode fall was in no case greater than four

TABLE V.

Potential Difference in Volts between the Cathode and Points in the Gas at a given Number of Mean Free Paths from it. Aluminum Cathode in Oxygen. For Twice Normal Current Density: $j\bar{\lambda}^2 = .162$

Gas Pressure (mm.).	Number of Mean Free Paths.					
	2	3	5	6	7	8
1.52	256	292	322	324	325	325
1.84	240	276	318	323	323	323
2.06	252	286	320	325	325	325
2.25	256	287	317	322	323	323
2.26	256	287	318	——	326	326
2.35	260	292	320	324	326	326
2.39	262	290	320	324	325	324
2.46	260	291	320	324	324	324
2.48	264	294	320	326	327	326
2.94	253	288	320	325	327	327
3.02	258	286	320	325	326	327
3.05	259	291	320	326	328	328
Means:	259	288	320	324	325	325

TABLE VI.

Potential Difference in Volts between the Cathode and Points in the Gas at a given Number of Mean Free Paths from it. Aluminum Cathode in Oxygen. For Four Times Normal Current Density: $j\bar{\lambda}^2 = .324$

Gas Pressure (mm.).	Number of Mean Free Paths.				
	2	3	4	5	6
1.43	306	338	346	348	348
1.97	302	338	351	356	356
2.07	300	345	359	367	366
2.23	312	343	352	361	362
2.24	312	348	360	361	361
Means:	306	342	353	359	359

per cent.—always an increase and greater for the larger current. An inspection of these tables warrants the conclusion that the potentials

are practically independent of the gas pressure; hence their means are taken as representative. These means are plotted in Fig. 2 (circles) using the potential differences as ordinates and the number of mean free paths from the cathode as abscissæ. They show, as in hydrogen, a marked decrease in distance to the point of minimum gradient (at x_0, see Fig. 2) as the current density is increased.

Mobility of the Positive Ions.—To the above data we may apply the theoretical deductions for calculating the upper and lower limits for the mobility of the positive ions. This is defined as the velocity in centimeters per second of the ion in unit field. Skinner gives[1] the two inequalities:

$$V_0 - V < \left[\left(\frac{16\pi j}{9\overset{+}{\mu}}\right)^{\frac{1}{3}}(x - x_0)\right]^{\frac{3}{2}}$$

$$> \left[\left(\frac{16\pi j}{9\overset{+}{\mu}}\right)^{\frac{1}{3}}(x - x_0) - \epsilon^{\frac{3}{2}}\right]^{\frac{2}{3}} + \epsilon$$

where $V_0 - V$ is the difference in potential between the point of minimum gradient at x_0 in the negative glow and any other point x nearer the cathode; j the current density, $\overset{+}{\mu}$ the mobility of the positive ions and ϵ the ionizing potential of the gas all expressed in c.g.s.-e.s. units. The upper and lower limits of $\overset{+}{\mu}$ may be calculated by making equations of the above inequalities and by substituting the observed values in their proper units. For the first we write:

$$V_0 - V_1 = \left(\frac{16\pi j}{9\overset{+}{\mu}}\right)^{\frac{1}{2}}(x_1 - x_0)^{\frac{3}{2}} \tag{1}$$

The second may be transformed as follows:

$$V_0 - V_1 - \epsilon = \left[\left(\frac{16\pi j}{9\overset{+}{\mu}}\right)^{\frac{1}{3}}(x_1 - x_0) - \epsilon^{\frac{3}{2}}\right]^{\frac{2}{3}}$$

$$(V_0 - V_1 - \epsilon)^{\frac{3}{2}} + \epsilon^{\frac{3}{2}} = \left(\frac{16\pi j}{9\overset{+}{\mu}}\right)^{\frac{1}{3}}(x_1 - x_0) \tag{2}$$

$$[(V_0 - V_1 - \epsilon)^{\frac{3}{2}} + \epsilon^{\frac{3}{2}}]^3 = \left(\frac{16\pi j}{9\overset{+}{\mu}}\right)(x_1 - x_0)^3.$$

In the plot (Fig. 2) are indicated the positions of minimum gradient x_0. These are 9.5 mean free paths for "normal"; 6.6 for "twice normal" and 5.0 for "four-normal." The corresponding values of the potential; V_0 were taken from Tables IV., V. and VI. The position x_1 was chosen at two mean free paths from the cathode which also determines V_1 from the tables. The value of ϵ for oxygen is given by Franck and

[1] *L. c.*, June, p. 488.

Hertz[1] as 9 volts. Expressing these quantities and also the current in c.g.s.-e.s. units and substituting in (1) and (2) we have calculated the upper and lower values of $\mathring{\mu}$. They do not differ greatly. Their mean for a pressure of 1 mm. was found to be 1.47×10^6 cm. per sec. for a field of 1 c.g.s.-e.s. unit or, in a field of one volt per cm. 4.9×10^3 cm. per sec.—about five times the value customarily obtained. For hydrogen Skinner obtained 2.7×10^4 cm. per sec. for one volt per cm.—about six times the accepted magnitude under ordinary measurements.

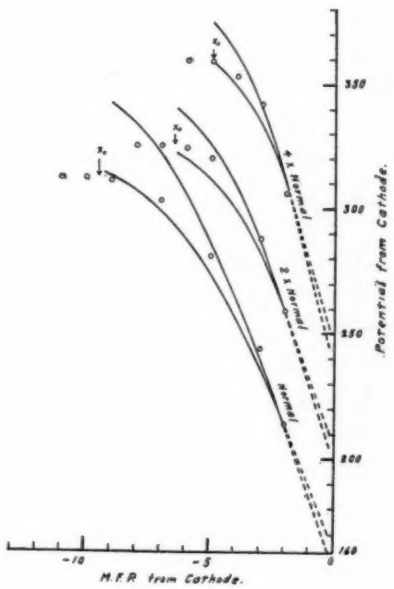


Fig. 2.

Using the above mean for the value of $\mathring{\mu}$, the same values for x_0, and the potentials at two mean free paths from the cathode as a starting point, we have determined from (1) and (2) the theoretical curves between which the observed values should fall. The calculated and observed potentials are tabulated in Table VII.—starting points in italics. The corresponding curves with their extensions to the cathode in broken lines are shown in Fig. 2. Referring to this figure, we find the observed

TABLE VII.

Calculated and Observed Potential Differences between Cathode and Points in the Gas at a given Number of Mean Free Paths from it. Aluminum in Oxygen.

Number of Mean Free Paths.	Calculated from Equation 1.	Calculated from Equation 2.	Observed.
For Normal Current Density: ($j = 1.33 \times 10^6$ c.g.s.-e.s.)			
0.2	163	170	—
2.	*214*	*214*	*214*
3.	240	236	244
4.	264	256	—
5.	285	274	281
6.	305	287	—
7.	322	299	303
9.3	344	314	312

[1] J. Franck and G. Hertz, Ber. d. Deutsch. Phys. Ges., 2, 1913, p. 34.

TABLE VII.

Calculated and Observed Potentiat Differences between Cathode and Points in the Gas at a given Number of Mean Free Paths from it. Aluminum in Oxygen.

Number of mean Free Paths.	Calculated from Equation 1.	Calculated from Equation 2.	Observed.
For Twice Normal Current Density: ($j = 2.66 \times 10^6$ c.g.s.-e.s.)			
0.2	205	210	—
2.	*259*	*259*	*259*
3.	285	281	288
4.	308	299	—
5.	326	—	320
6.4	340	322	325
For Four Times Normal Current Density: ($j = 5.32 \times 10^6$ c.g.s.-e.s.)			
0.2	245	252	—
2.	*310*	*310*	306
3.	339	334	342
4.	362	349	353
5.	374	359	359

values falling fairly consistently between the theoretical limits; but with a gradient (or slope) near the negative glow distinctly lower than either.

The Immediate Cathode Fall.—From the fact that the difference of potential between the cathode and any definite number of mean free paths from it is simply a function of $j\bar{\lambda}^2$ it must follow that the difference of potential between the cathode and the gas immediately adjacent to it, is also a function of $j\bar{\lambda}^2$. The theory assumes this fall to take place over a distance equal to one mean free path of the positive ions from the cathode—approximately .2 mean free path of the electrons. By extending the theoretical curves up to this point, a calculated value for this " immediate fall " at the cathode may be obtained. The following table gives the mean values V_b of this immediate fall. They show that V_b

V_b	Ratios.	$(j\bar{\lambda}^2)^{.30}$	Ratios.
167	1.	.470	1.
208	1.24	.592	1.26
249	1.49	.713	1.52

is closely proportional to $(j\bar{\lambda}^2)^{.30}$. Skinner found with hydrogen that V_b is proportional to $(j\bar{\lambda}^2)^{.38}$.

The Electron Current from the Cathode.—For obtaining the ratio of the

electron current to the total current, Skinner has derived the following equation.[1]

$$\frac{\bar{j}_k}{j} = \frac{\bar{\mu}}{\bar{\mu} + \dot{\mu}} \cdot 2^{-\left[\frac{x_k - x_a}{\bar{\lambda}} + \frac{V_0 - V_a}{\epsilon}\right]} \qquad (3)$$

in which $\bar{\mu}$ and $\dot{\mu}$ are respectively the mobilities of the negative and positive ion in the negative glow; $\bar{j}_k$ the electron current density at the cathode; j the total current density; $(x_k - x_a/\bar{\lambda})$ the number of mean free paths between the cathode and the point where ionization ceases to take place at every mean free path: $V_0 - V_a$ the fall between this point and the negative glow; and ϵ the ionizing potential of the gas. This relation was obtained by assuming that each electron leaving the cathode resulted in two electrons at the end of the first mean free path, four at the end of the second, eight at the end of the third, and so on for the region in which the potential difference per mean free path was equal to or greater than the ionizing potential; and, in the region where the potential gradient was lower than this, ionization was assumed to occur each time an electron moved through a potential difference equal to ϵ. Assuming $\bar{\mu}$ and $\dot{\mu}$ equal, the ratios of $\bar{j}_k/j$ for the three current densities are as follows:

Current Density.	$\left(\frac{x_k - x_a}{\bar{\lambda}}\right)$	$\left(\frac{V_0 - V_a}{\epsilon}\right)$	$\left(\frac{\bar{j}_k}{j}\right)$
Normal.....	7	1.0	2.0×10^{-3}
2×normal.....	5	.6	$10.\times10^{-3}$
4×normal.....	4	.7	$19.\times10^{-3}$

Observations on the extent of the cathode dark space in oxygen show that there is no perceptible change with large changes in current density.

Nitrogen.

Atmospheric nitrogen was obtained by passing air slowly over heated phosphorous. The gas was then allowed to stand over crushed potassium hydrate and phosphorous pentoxide to remove the carbon dioxide and moisture. Finally the last traces of oxygen were removed by heating the gas for a time in a tube coated on the inner surface with an electrolytic deposit of sodium which had been previously accumulated by sending an electric current from a sodium amalgam bath through the heated walls of the tube.[2] It is very important that no oxygen be present for as Warburg as shown and I also have observed, even a trace will vitiate results by giving an abnormally high cathode fall.

[1] *L. c.*, August, p. 163.

[2] E. Warburg, Wied. Ann., 40, 1890, p. 1.

Current Density and Number of Mean Free Paths to the Negative Glow with Normal Cathode Fall.—A series of observations with an aluminum cathode in Nitrogen is given in Table VIII. As in the case of oxygen, each pressure represents a fresh gas filling. There was considerable difficulty in obtaining satisfactory observations in nitrogen, because with each new gas filling, the cathode fall was usually distinctly larger than with the preceding filling. At most, only three fillings could be used before it became necessary to remove the electrode and repolish it. Unlike the other gases the cathode fall showed, however, a decrease with duration of the discharge in the same filling—especially noticeable if the electrode had not been previously cleaned. This was attributed to the presence of freed hydrogen. The mean, 218 volts, of the values given in Table VIII., column 2 is about five per cent. higher than the fall as given by Warburg, 207 volts.[1] It agrees closely, however, with Skinner's value,

TABLE VIII.

Aluminum Cathode in Nitrogen. Area of Cathode: 3.04 sq. cm.

Gas Pressure (mm.).	Normal Cathode Fall (Volts).	Normal Current Density, j_n.	Distance to Neg. Glow, $x_k - x_0$.	Mean Free Path, $\bar{\lambda}$.	$j_n\bar{\lambda}^2$	$\frac{x_k - x_0}{\bar{\lambda}}$
1.43	216	.29 ma.	3.30 mm.	.28 mm.	.023	11.8
1.78	——	.39	2.90	.23	.021	11.0
1.81	213	——	2.54	.225	——	11.1
2.30	220	.72	2.32	.18	.023	12.8
2.32	219	.76	2.08	.175	.023	12.0
2.41	219	.76	2.10	.17	.022	12.3
2.53	220	.92	1.80	.16	.024	11.2
2.69	214	.99	1.90	.15	.022	12.6
2.91	218	1.08	1.70	.14	.021	12.1
2.96	220	1.12	1.85	.14	.022	12.8
3.30	216	1.45	1.54	.12	.021	12.5
3.33	212	1.58	——	.12	.023	——
3.59	222	1.81	1.47	.115	.024	——
4.07	218	——	1.22	.10	——	12.0
4.49	223	2.46	1.15	.091	.021	12.1
Mean	218			Mean	.0223	12.0
Max. dev.	3%			Max. dev.	9%	8%
Mean dev.	1%			Mean dev.	5%	4%

217 volts.[1] There was some hesitation in the glow covering the cathode when the current was first started. The normal current densities given in column 3, represent the minimum which would cover the cathode after the discharge had first been forced over the whole face. This minimum sometimes showed a tendency to rise, depending on how much the gas

[1] C. A. Skinner, Phil. Mag., 6, VIII., p. 387.

pressure had been increased by the gases freed from the metal. This pressure increase during a set of readings was never more than four per cent. The normal current density for any given gas pressure of nitrogen is about twice that for hydrogen and about one third that for oxygen; $j_n\overline{\lambda}^2$ (column 6) is approximately one half that in hydrogen and one fourth that in oxygen. The number of mean free paths from the cathode to the negative glow (column 7) lies between the values for hydrogen and oxygen.

Potential Curves in the Region between the Cathode and the Negative Glow.—Table IX. gives observations on the differences of potential between the cathode and successive points in the gas, using an aluminum cathode in nitrogen with the three current densities " normal," " twice normal ", and " four-normal." Each series, except the last (at " four-

TABLE IX.

Potential Difference in Volts between the Cathode and Points in the Gas at a given Number of Mean Free Paths from it. Aluminum in Nitrogen.

Gas Pressure (mm.).	Number of Mean Free Paths.							
	2	3	5	7	9	10	11	12
For Normal Current Density: $j\overline{\lambda}^2=.022$								
1.38	129	151	187	213	221	224	226	226
2.06	117	135	167	195	213	218	222	223
2.17	132	148	178	199	211	215	216	217
2.57	130	151	178	196	206	209	210	211
2.63	131	149	181	207	222	226	229	231
2.65	129	147	177	196	209	212	213	215
2.92	119	136	164	191	210	217	221	222
3.86	130	148	175	195	210	216	220	223
Means	127	146	176	199	213	217	220	221

Gas Pressure (mm.).	Number of Mean Free Paths.					
	2	4	6	7	8	9
For Twice Normal Current Density: $j\overline{\lambda}^2=.044$						
2.22	155	194	219	229	235	236
2.23	148	184	211	220	224	224
2.24	142	180	204	212	217	218
2.55	156	195	222	229	234	234
2.70	153	190	214	223	228	229
Means	151	189	214	223	228	228
For Four Normal Current Density: $j\overline{\lambda}^2=.088$						
2.46	173	214	238	242	242	—

normal") was taken in a fresh gas filling. The large increase in the cathode fall with successive fillings, however, made it impossible to obtain comparative results with four-normal current density with fresh gas fillings as has been the plan followed with other gases. Comparing the different gases, it is found that oxygen and hydrogen both show a greater relative rise in the cathode fall with the same multiple of normal current density. Here as in the other gases, potentials are independent of the gas pressures, and the point of minimum gradient draws in toward the cathode as the current density is increased. The means are plotted as circles in Fig. 3.

Some years ago Skinner found[1] that after passing a heavy current through nitrogen the potential difference between cathode and probe was practically the same for all positions of the probe between the cathode and the negative glow. My observations have shown, however, in all cases a marked gradient in this region. It is very probable that the heavy preliminary current used by Skinner simply served to render (by cathode spray) the insulating sheath of his probe conductive, the potentials indicated being then practically those of the highly conductive negative glow through which the probe passed.

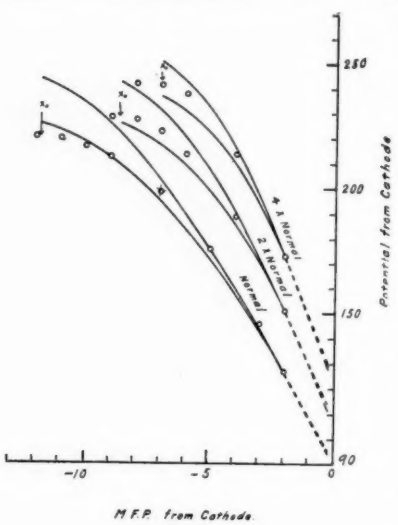


Fig. 3.

Mobility of the Positive Ions.—The mobility $\overset{+}{\mu}$ for the positive ions was calculated from equations (1) and (2) by the same method as used for oxygen. A mean value of 3.1×10^3 cm. per sec. in a field of one volt per cm. was thus obtained. It is rather surprising to find this only about six-tenths that of oxygen—when ordinary measurements show them to be about the same. Using this value, the theoretical curves shown in Fig. 3 were computed. The results are incorporated in Table X.

The Immediate Cathode Fall.—This obtained in the same way as for oxygen (at .2 mean free path from the cathode) is proportional to $(j\bar{\lambda}^2)^{.25}$ approximately; as appears from the table on page 267.

Magnitude of the Electron Current from the Cathode.—The ionizing potential for nitrogen was used as 7.5 volts.[2] Substituting in equation

[1] C. A. Skinner, Phil. Mag., [6], 2, 1901, p. 616.

[2] J. Franck and G. Hertz, Ber. d. Deutsch. Phys. Ges., 2, 1913, p. 34.

TABLE X.

Calculated and Observed Potential Differences between Cathode and Points in the Gas at a Given Number of Mean Free Paths from it. Aluminum in Nitrogen.

Number of Mean Free Paths.	Calculated from Equation 1.	Calculated from Equation 2.	Observed.
For Normal Current Density: ($j = 4.02 \times 10^5$ c.g.s.-e.s.)			
0.2	94	95	—
2.	*127*	*127*	*127*
3.	144	143	146
5.	177	172	176
7.	204	196	199
9.	226	213	213
10.	235	218	217
11.8	244	226	220
For Twice Normal Current Density: ($j = 8.04 \times 10^5$ c.g.s.-e.s.)			
0.2	111	114	—
2.	*151*	*151*	*151*
4.	190	185	189
6.	220	210	214
7.	232	217	223
8.6	243	226	228
For Four Times Normal Current Density: ($j = 12.06 \times 10^5$ c.g.s.-e.s.)			
0.2	128	129	—
2.	*173*	*173*	*173*
4.	215	210	214
5.	232	221	230
6.	244	230	238
7.	251	237	242

V_b	Ratios.	$(j\bar{\lambda}^2)^{.25}$	Ratios.
94.5	1.	.387	1.
112.5	1.19	.460	1.19
128.5	1.36	.546	1.41

(3), as before, to obtain the ratio of the electron current at cathode to the total current the results are as follows:

Current Density.	$\left(\frac{x_k - x_a}{\bar{\lambda}}\right)$	$\left(\frac{V_0 - V_a}{\epsilon}\right)$	$\left(\frac{\bar{j}_k}{j}\right)$
"Normal"	7	2.8	$6. \times 10^{-4}$
2 "	7	.7	$24. \times 10^{-4}$
4 "	6	.5	$55. \times 10^{-4}$

These values are somewhat higher than those obtained by Skinner for hydrogen and very much less than those for oxygen.

Observations on the extent of the cathode dark space in nitrogen showed a marked decrease with increasing current density. For example if it extends 6 mean free paths from the cathode at normal current density,

it decreases to about 4.5 mean free paths at four times normal current density.

SUMMARY.

To facilitate comparison the various magnitudes measured by Skinner in hydrogen with an aluminum cathode and those obtained in nitrogen and oxygen with the same metal are summarized in the following table:

Gas.	Cathode Fall.	$(\overline{\lambda^2})$	$\left(\frac{x_k - x_0}{\overline{\lambda}}\right)$	Immediate Cathode Fall.	Mobility of Positive Ions, at 1 mm. Gas Pres.	$\left(\frac{\overline{j_k}}{j}\right)$
For Normal Current Density.						
H	197	.038	15.3	78.	27.0×10^3	$4.\times10^{-4}$
N	218	.022	12.0	95.	3.1×10^3	$6.\times10^{-4}$
O	311	.081	10.6	168.	4.9×10^3	$20.\times10^{-4}$
For Twice Normal Current Density.						
H	204	.076	12.	101.	———	$15.\times10^{-4}$
N	228	.044	8.	112.5	———	$24.\times10^{-4}$
O	325	.162	7.	207.5	———	$100.\times10^{-4}$
For Four Times Normal Current Density.						
H	227	.152	10.	130.	———	$42.\times10^{-4}$
N	242	.088	7.	128.5	———	$55.\times10^{-4}$
O	359	.324	5.	248.5	———	$190.\times10^{-4}$

To conclude it is found for each of the different gases, hydrogen, nitrogen and oxygen, that all pressures giving the normal cathode fall have the same number of mean free paths to the point of minimum potential gradient in the negative glow, and have a normal current density proportional to the square of the gas pressure.

With normal current density the cathode fall is a minimum. As the current density is increased the immediate cathode fall also increases, but the fall over the remaining distance to the negative glow decreases. This decrease in the gas is due to the higher ratio of the electron current from the cathode to the total current, which reduces the distance from the cathode to where the negative charge in the gas equals the positive.

Finally, the difference in potential between the cathode and any point at a definite number of mean free paths from it is a function of the product of the current density into the square of the mean free path of the electron, *i. e.*, a function of the ratio of the current density to the square of the gas pressure.

I wish to express my indebtedness to Prof. Skinner, who suggested the problem, and under whose direction it has been my privilege to work, and also to Dr. J. T. Tate for valuable assistance in the experimental part.

THE BRACE LABORATORY OF PHYSICS,
UNIVERSITY OF NEBRASKA,
June, 1915.

TESTS OF THERMO-ELECTRIC FORMULÆ BASED ON BISMUTH AND BISMUTH-TIN ALLOYS.

BY A. E. CASWELL.

INTRODUCTION.

IN a previous paper[1] the writer pointed out the fact that the development of the electron theory made trustworthy determinations of the Peltier E.M.F. desirable. The experimental work outlined in this paper is a continuation of the previous work, but the present apparatus was designed to measure not only the Peltier E.M.F., but the Thomson E.M.F. and thermo E.M.F. as well. The metals used were bismuth and alloys of bismuth and tin containing less than ten per cent. tin. The latter part of this paper is devoted to a study of the electron theory of thermo-electricity, as developed by different individuals, in the light of experimental facts, from which it appears (1) that the formulæ proposed by Drude[2] are verified by experiment, and (2) that the electrons which take part in thermo-electric phenomena are identical with those which take part in the conduction of electricity and heat in metals.

THE PELTIER EFFECT.

The method here employed in the measurement of the Peltier E.M.F. was that devised by Barker and myself and referred to in my previous paper as the "First Method." The apparatus was modified, however, so as to adopt it to the measurement of the Thomson E.M.F. Since it is proposed to deal with the latter subject in a future paper, a description of the apparatus will not be given here further than to point out minor modifications tending to increase the accuracy of the work and to facilitate the operations. For a more detailed description of the apparatus the reader is referred to my previous paper.

The Dewar flasks, used as calorimeters, were mounted in a wooden frame, the top of which was flush with the tops of the flasks. A thick layer of felt was placed around the upper end of each flask between the flask and the frame so that it extended slightly above the top of the flask. In order to adapt the apparatus to the measurement of the Thomson E.M.F. two couples, connected in parallel, were used instead of one.

[1] PHYS. REV., Ser. I., XXXIII., pp. 379–402, Nov., 1911.

[2] Drude, Ann. der Phys., 1, p. 590, 1900.

Each couple consisted of an inverted U-shaped casting of bismuth or one of the alloys, the sides and bottom of the U being about 19 cm. long, the cross-section about 20 sq. mm., connected to heavy copper leads by means of spring binding-posts. These facilitated the substitution of one specimen for another. The compensating resistance coils were single loops of No. 38 manganin wire about 7 cm. long, and having resistances of 3.529 and 3.655 ohms, respectively. These were soldered to heavy copper leads. The rotary stirrers previously used were replaced by ones having a vertical reciprocating motion. These have proven quite as satisfactory and have saved considerable time in the way of adjustment. Everything which went inside of the flasks was securely fastened to a board, the under side of which was completely covered with a heavy layer of felt. The vertical portions of the castings and the stirrer rods passed through holes in the board and a second layer of felt on the upper side of the board. A third layer of felt covered the horizontal portions of the castings, the only openings in this layer being for the stirrer rods. When this board was put in place and bolted to the frame the felt provided complete heat insulation except at the stirrer rods, which rods passed through snugly fitting holes in three layers of felt, each of which was about one cm. thick.

The ammeters used were carefully calibrated. The bismuth was C. A. F. Kahlbaum's reagent bismuth and the tin Kahlbaum's purified tin. These were fused together in an electric furnace and well stirred at a temperature not far above the melting-point of bismuth, care being taken to prevent the alloy becoming contaminated with an oxide of the metals. The first and second columns of Table I. give the percentages of tin, by weight, in three alloys and the corresponding Peltier E.M.F.'s between the alloys and copper, also the Peltier E.M.F. between the pure bismuth and copper. The latter value is somewhat greater than that given in my previous paper. The difference is probably accounted for by a slight impurity in the sample of bismuth previously used. The value given in the table is in each case the mean of several determinations, and the probable error varies between one and two per cent. The mean temperature of these experiments was 20.7° C. or 293.5° K.

In the third column of this table the values of the ratio, n_1/n_2, of the number of electrons taking part in thermo-electric phenomena in the case of an alloy to the corresponding number in the case of pure bismuth are given, these values being computed from Drude's formula. In the fourth column the values of the same ratio as computed from Thomson's formula are given.

THERMO E.M.F.

The thermo E.M.F. between these specimens and copper was determined in each case by heating the liquid in one of the calorimeters to a temperature about ten degrees above the other, which was kept at the temperature at which the Peltier experiments were carried out. The ratio of the thermo E.M.F. of the copper-specimen couple to that of the four copper-constantan couples in series, which were used to determine the equality of the temperatures in the two calorimeters during the Peltier experiments, was obtained with the aid of a potentiometer. The thermo-electric power of the copper-constantan couples was then determined absolutely, the value found agreeing within the limits of experimental error with that given in Kaye and Laby's tables, viz., 41.8 microvolts per Centigrade degree. The values of the thermo-electric power given in the fifth column of Table I. were obtained by multiplying this number by four times the ratio mentioned above.

The sixth and seventh columns of Table I. correspond, respectively, to the third and fourth columns, the equations used in these cases being those for thermo-electric power instead of Peltier E.M.F. The close agreement between the numbers in the third and sixth columns and between those in the fourth and seventh columns of this table depends upon the use of Lord Kelvin's equation $P = QT$, where P is the Peltier E.M.F., Q is the thermo-electric power, and T is the absolute temperature. In a way this relation serves to check the accuracy of the experimental work, provided we are willing to assume the validity of the second law of thermodynamics. If we are in doubt on this point the experimental facts should convince us of the validity of the law. I mention this point because of two facts. The first is that the validity of the law has been called in question recently. The second is that if this law is true, and if the quantities which are actually measured are those referred to in this equation based on the law, then it would seem unnecessary to carry out experiments on both Peltier E.M.F. and thermo E.M.F. since the second set of experiments would add no new information. Both of these conditions, I believe, are fulfilled.

TABLE I.

Per Cent. Tin.	Peltier E. M. F. in Millivolts.	n_1/n_2 Drude.	n_1/n_2 Thomson.	Thermo-electric Power in Microvolts per °C.	n_1/n_2 Drude.	n_1/n_2 Thomson.
0	+19.35	1.000	1.000	+67.2	1.000	1.000
3.75	−10.87	0.550	0.303	−35.4	0.552	0.304
6.36	−11.67	0.542	0.293	−42.7	0.528	0.279
9.93	−10.45	0.555	0.308	−38.0	0.543	0.295

Curve I. in Fig. 1 is plotted from the data in the first and third columns of this table, curve II. from the data in the first and sixth columns.

It will be observed that the density of the electrons in copper lies between the density in bismuth and that in any of the alloys experimented upon.

THEORETICAL CONSIDERATIONS.

According to the electron theory as developed by Drude the Peltier E.M.F. between two metals should be given by the equation

$$P = \frac{4\alpha T}{3e} \log \left(\frac{n_1}{n_2}\right),$$

where P is the Peltier E.M.F., α is a universal constant, the ratio of the kinetic energy of a molecule to the corresponding absolute temperature T, e is the charge on an electron, n_1 is the number of electrons which take part in thermo-electric phenomena per unit volume of the first metal, and n_2 is the corresponding number for the second metal. If the current flows from the metal in which n is large to that in which n is small, then heat will be absorbed at the junction. The equation given above is equivalent to the equation.

$$P = \frac{2RT}{e} \log \left(\frac{n_1}{n_2}\right),$$

where R is the gas constant for a gram-molecule of a gas and is equal to 8.315 joules per Centigrade degree, and e is the electrochemical equivalent of hydrogen and is equal to 96,470 coulombs per gram.

Similarly, if Q is the thermo-electric power, then

$$Q = \frac{2R}{e} \log \left(\frac{n_1}{n_2}\right),$$

in conformity with the relation $P = QT$.

J. J. Thomson[1] and O. W. Richardson[2] have deduced formulæ identical with the above providing the factor 2 is omitted. Drude's calculation is based upon the assumption of a convective equilibrium between the diffusion of the electrons due to the difference in concentration and the opposing flow of electrons due to a difference in potential thus set up. Thomson assumes that the electrons are in equilibrium under the electric force and the opposing pressure gradient at the boundary. Richardson assumes that the electric current in metals is carried by electrons which are dynamically equivalent to the molecules of a gas, and that the po-

[1] "Corpuscular Theory of Matter," p. 74.

[2] Phil. Mag., [6], Vol. XXIII., p. 269, 1912.

tential energy of an electron is less when inside an uncharged conductor than when it is at a considerable distance outside. This difference in potential energy is due to a force at the interface which tends to hold the electrons in the conductor. The final test of the correctness of any of these assumptions is an experimental one.

At the beginning of this paper it was stated that the experimental facts seemed to agree with the formulæ of Drude rather than those of Thomson and Richardson. If such is the case, it appears that Drude's position is the correct one. It remains to justify that statement. It is obviously necessary to obtain from other sources reliable values of the ratio n_1/n_2. Such values can be obtained from the work of Schulze[1] on the electrical and thermal conductivities of bismuth and its alloys, providing we make two assumptions. The first is that the mean free path of the electrons, l, has practically the same value in a pure metal and in an alloy of that metal containing only a very small percentage of a second metal. The second assumption is that the electrons which take part in thermo-electric phenomena are identical with those which take part in the conduction of electricity and heat in metals. In most cases the assumption of the equality of the mean free paths of the electrons in two different metals would be unwarranted. In the case of a bismuth-tin alloy containing only a small percentage of tin, the density of the alloy not being very far different from that of pure bismuth, the average spacing of the molecules cannot be very far different from that in the pure metal, even though the number of molecules of tin present may suffice to destroy the crystalline structure characteristic of bismuth. The case is very similar to that of mixing a quantity of shot of one size with a very much larger quantity of shot of a different size. Neither the number of shot in a unit volume of the mixture, nor the average distance between centers, will differ to any marked extent from the corresponding values for the larger quantity of shot alone. It therefore follows that although we cannot assert the exact equality of l_1 and l_2, where the subscript 1 refers to the alloy and the subscript 2 to the pure bismuth, we feel confident that the assumption of this equality, doubtless slightly contrary to fact, cannot introduce into our calculations an error of more than a very few per cent. This point will be referred to again. It is not obvious that the electrons involved in electrical and thermal conductivity are identical with those involved in thermo-electricity. On the other hand, there is no *a priori* reason for denying such identity. The assumption is a simple one; it does no violence to the experimental facts, but instead serves to link together such facts in different portions

[1] Ann. der Phys., 9, pp. 555–589, 1902.

of the subject of physics; we are, therefore, justified in making it. An alternative would be to assume the validity of one of the proposed formulæ. If we assume the validity of Drude's formula, the calculated values of the ratio n_1/n_2 are such that one is led to the conclusion that the same electrons take part in the phenomena of conduction and thermo-electricity. If the validity of any other formula is assumed, no relation which we might reasonably expect is found.

If we assume that the specific electrical conductivity, σ, is given correctly by the equation

$$\sigma = \frac{ne^2lv}{6RT},$$

where n, e, l, R, and T, have the same meanings as before, and v is the mean square velocity of the electrons, which depends only upon the temperature; then the ratio of the electrical conductivities of two metals at the same temperature is given by the equation

$$\frac{\sigma_1}{\sigma_2} = \frac{n_1 l_1}{n_2 l_2}. \tag{1}$$

If, in addition, we assume that $l_1 = l_2$, then equation (1) becomes

$$\frac{\sigma_1}{\sigma_2} = \frac{n_1}{n_2}. \tag{2}$$

Similarly, if we assume that the specific thermal conductivity, k, is given correctly by the equation $k = \frac{1}{2}nlvR$, then it follows that

$$\frac{k_1}{k_2} = \frac{n_1}{n_2}, \tag{3}$$

The fifth and sixth columns of Table II. give the values of the ratio n_1/n_2 computed from Schulze's data on electrical and thermal conductivities, using equations (2) and (3), respectively. The fourth column gives the corresponding percentages, by weight, of tin. For the sake of comparison the data given in the first, third and sixth columns of Table I. is repeated in the first three columns of this table. In Fig. 1 the values of the ratio n_1/n_2 are plotted as ordinates and the corresponding percentages of tin as abscissae. The curves I., II., III. and IV are for Peltier E.M.F., thermo-electric power, electrical conductivity and thermal conductivity, respectively.

An examination of the data in Table I., or of the curves in Fig. 1, reveals the fact that the data obtained from the Peltier E.M.F. agree with those obtained from the thermo-electric power within the limits of

Table II.

Showing the values of the ratio n_1/n_2 obtained from different sources.

Per Cent. Tin.	Peltier E.M.F.	Thermo-electric Power.	Per Cent. Tin.	Electrical Conductivity.	Thermal Conductivity.
0	1.000	1.000	0	1.000	1.000
——	——	——	0.34	0.717	0.741
——	——	——	0.71	0.610	0.667
3.75	0.550	0.552	2.15	0.543	0.578
6.36	0.542	0.528	7.43	0.588	0.662
9.93	0.555	0.543	—	——	——

probable experimental error. Furthermore, there is substantial agreement between the data obtained from the above-mentioned sources and those obtained from either electrical or thermal conductivity, when the percentage of tin is less than, say, four per cent. My values of the ratio n_1/n_2 for 3.75 per cent. tin lie between the values deduced from the electrical and thermal conductivities. Yet the coincidence of the latter

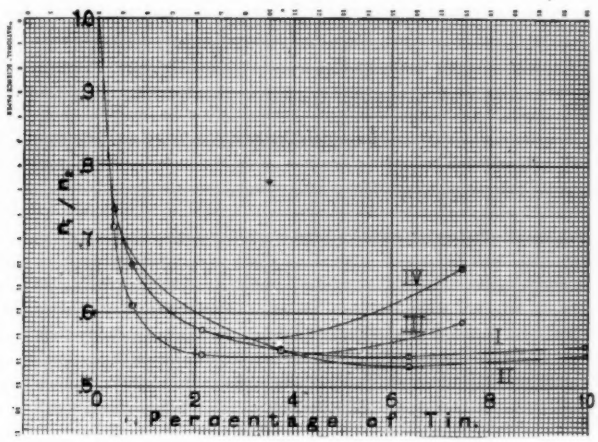


Fig. 1.

values is fundamental to the Wiedemann-Franz law. With larger percentages of tin curves III. and IV. diverge rather rapidly from curves I. and II. This is what we should expect since the value of l_1 must become greater than l_2 as the percentage of tin is increased. The conductivity of tin is greater than that of bismuth, but the density of the electrons is less in tin than in bismuth. The difference in conductivity must be accounted for by a greater mean free path of the electrons in tin than in bismuth. When the difference between l_1 and l_2 begins to be appreciable the curves III. and IV. begin to diverge from the curves I. and II., and this divergence might be used to determine the relative values of l_1

and l_2. The writer believes that the logical conclusions to which a study of the experimental facts leads are two, viz., (1) that Drude's thermo-electric formulæ agree with the experimental facts, and (2) that the same electrons take part in thermo-electric phenomena and in the conduction of electricity and heat in metals.

If we adopt the Thomson formulæ, we must deny either one or both of the assumptions made in the preceding discussion. Let us deny the equality of l_1 and l_2, and assume the identity of the electrons. A comparison of the data given in the fifth and sixth columns of Table II. with the data given in the fourth and seventh columns of Table I. shows that $(l_1 n_1/l_2 n_2)^2$ is approximately equal to N_1/N_2, where n is the number of electrons taking part in conduction and N is the number taking part in thermo-electric phenomena. But if $n = N$, then it follows that $(l_1/l_2)^2$ is approximately equal to n_2/n_1, or N_2/N_1. Since the value of l depends upon collisions with molecules rather than electrons, l should not vary with n except in so far as each varies with the concentration and kind of the molecules. A decrease in the value of n might correspond to a decrease in the concentration of the molecules and a corresponding increase in the mean free path of the electrons. From the values of the ratio N_1/N_2 and the relation stated above, it appears that the mean free path of an electron in one of these alloys would have to be about 1.8 times that in pure bismuth in order to satisfy Thomson's formulæ. Such a difference in the mean free path must correspond to a marked difference in the distance between the molecules and, consequently, to a marked difference in the density. Such a marked difference in density does not exist. If we assume $l_1 = l_2$, Thomson's formulæ lead to the relation

$$\frac{N_1}{N_2} = \left(\frac{n_1}{n_2}\right)^2.$$

This is a somewhat unique and, as it seems to me, an improbable relation. The third alternative is to deny both assumptions, in which case the agreement between Schulze's data and my own becomes merely an amazing coincidence.

The writer is aware that some may object to any line of reasoning based upon a metal such as bismuth which is difficult to obtain in the pure state, and perhaps on that account is abnormal in its behavior, and upon alloys which, generally speaking, have proven rather refractory when efforts have been made to reconcile their behavior with the simple assumptions of the electron theory. In all the work upon which our calculations are based unusual precautions were taken to insure the

purity of the metals. And so far as the writer is aware such special assumptions as may be necessary to explain the unusual behavior of alloys, or of pure bismuth, would not affect the conclusions reached in this discussion.

CONCLUSIONS.

The conclusions which may be drawn from this paper are:

1. From the value of the thermo-electric power, or that of the Peltier E.M.F., between two metals and well-known physical constants the ratio of the concentrations of the electrons in the two metals which take part in the phenomena of thermo-electricity can be determined.

2. These electrons are identical with those which take part in the conduction of electricity and heat in metals.

3. The conductivity ratios of two metals are equal to the ratio of the products of the mean free path and the concentration of the electrons.

4. From the ratios mentioned in 1 and 3 it is possible to determine the ratio of the mean free paths of the electrons in the two metals.

This investigation is being continued and its scope extended.

In conclusion the writer wishes to acknowledge his indebtedness to Professor W. P. Boynton, who has been a constant source of inspiration, and to those students in the department who have assisted in the making of the apparatus.

PHYSICAL LABORATORY,
UNIVERSITY OF OREGON,
July, 1915.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE COLUMBUS MEETING.

THE eighty-first meeting of the American Physical Society was held at Columbus, Ohio, December 27–30, 1915. It was the annual meeting and a joint meeting with Section B of the A. A. A. S. Six sessions were held for the reading of papers. President Merritt presided, except on Wednesday afternoon, which was devoted to a special program of invited addresses arranged by Section B. Vice-president E. P. Lewis was in charge of this session. At the other five sessions the following sixty-three papers were presented:

A Mechanical Device for the Rapid Evaluation of Certain Variable Exponential Functions. IRWIN G. PRIEST, National Bureau of Standards, Washington.

On the Value of $\gamma = C_p/C_v$ For Hydrogen. KARL K. DARROW.

Deviation of Natural Gas from Boyle's Law. R. F. EARHART and S. S. WYER.

Preliminary Report on the Diffusion of Solids. C. E. VAN OSTRAND AND F. P. DEWEY.

On the Properties of Matter at Low Temperatures. JAKOB KUNZ. (By title.)

Pressures and Critical Lengths in the Collapse of Short Tubes. A. P. CARMAN. (By title.)

A Photographic Study of the Relative Velocity of Sound Waves of Different Intensities. ARTHUR L. FOLEY.

A Preliminary Investigation of an Explosion Wave in a Gas. J. B. DUTCHER.

An Attempt to Detect a Change in the Specific Heat of Selenium with a Change in the Illumination, and also with the Application of an Electric Field. L. P. SIEG.

Wind Velocity and Elevation. W. J. HUMPHREYS.

A Proposed Physical Method for Reducing Radiant Power and its Luminous Value. IRWIN G. PRIEST AND CHAUNCY G. PETERS.

The Coefficient of Total Radiation of a Uniformly Heated Enclosure. W. W. COBLENTZ AND W. B. EMERSON.

A Luminosity Curve Equation and its Application to the Black Body. E. F. KINGSBURY.

Black Body Brightness and the Mechanical Equivalent of Light. HERBERT E. IVES AND E. F. KINGSBURY.

The True Temperature Scale for Tungsten and its Emissive Powers at Incandescent Temperatures. A. G. WORTHING.

Color Temperature Scales for Tungsten and Carbon. EDWARD P. HYDE, F. E. CADY AND W. E. FORSYTHE.

The Infra-red Spectra of the Alkaline Earth Group. H. M. RANDALL.

The Pole Effect in a Calcium Arc. HENRY G. GALE AND WALTER T. WHITNEY.

The Reflecting Power of Alkali Metals in Contact with Glass, as Determined by the Photo-electric Cell. J. B. NATHANSEN.

The Refractive Indices of Hydrogen and Helium on Bohr's Theory. C. DAVISSON.

A Photographic Study of the Diffraction Ring System in the Shadow of a Sphere. MASON E. HUFFORD.

The Ionization Produced by a β-particle. ALOIS F. KOVARIK AND L. W. MCKEEHAN.

The Rôle Played by Gases in Photo-Electric Discharge. R. A. MILLIKAN AND WILMER H. SOUDER.

The Relation between the Pressure Effect and the Light Effect in Selenium Crystals. E. O. DIETERICH.

On the So-called Magnetic Rays of Righi. JAMES E. IVES.

The Absorption Coefficients of various Metals for High Frequency X-Rays. S. J. M. ALLEN.

The Distribution of Energy in the X-Ray Spectrum of Tungsten and Molybdenum at Constant Potential. A. W. HULL.

The Emission Quanta of Characteristic X-Rays. DAVID L. WEBSTER.

The Tribo-luminescence of Manganese-Zinc Compounds. With Demonstration. C. W. WAGGONER.

A New Law relating Ionization Pressure and Current in the Corona of Constant Potentials. EARLE H. WARNER.

Arcs in Gases between Non-consuming Electrodes. G. M. J. MACKEY AND C. V. FERGUSON.

The Hall Effect and Allied Phenomena in Rare Metals and Alloys. ALPHEUS W. SMITH.

Mechanical and Acoustical Impedance, and the Theory of the Phonograph. A. G. WEBSTER.

Further Experiments on the Impedance of Conical Horns. A. G. WEBSTER.

The Effect of Surface Films on Contact E. M. F.'s. R. A. MILLIKAN AND WILMER H. SOUDER.

A Resonance Method for Measuring the Phase Difference of Condensers. H. L. DODGE.

The Magnetic Susceptibility of Oxygen. W. P. ROOP. (Read by E. P. LEWIS.)

An Unrecognized Error in the Measurement of Magnetic Flux. ARTHUR WHITMORE SMITH.

Unipolar Induction and Absolute Rotation. E. H. KENNARD.

The Electrical Resistance of Vertically Suspended Wires. S. R. WILLIAMS.

A Simplified Apparatus for Measuring the Conductivity of Electrolytes. R. P. HIBBARD.

Measurements of an Electric Current from its Heating Effect. S. LEROY BROWN.

A Study of the Law of Response of the Silicon Detector. LOUISE S. MCDOWELL AND FRANCES G. WICK.

On the Free Vibrations of a Lecher System—IV. F. C. BLAKE AND CHARLES SHEARD.

Constant High Potential for X-Ray Work. ALBERT W. HULL.

Carbon Compression Rheostats. E. L. CLARK.

On the Theorem that all Action Requires Action at a Distance Somewheres. E. H. KENNARD.

The Black Body at the Melting Point of Platinum as a Fixed Point in Photometry. HERBERT E. IVES.

The Luminous Efficiency of the Carbon Incandescent Lamp and the Mechanical Equivalent of Light. HERBERT E. IVES AND E. F. KINGSBURY.

The Mobility of Positive Ions. HENRY A. ERIKSON.

The Hall Effect and Allied Phenomena in Tellurium. P. I. WOLD.

A Wehnelt Cathode Ray Tube Magnetometer. C. T. KNIPP AND L. A. WELO.

An Investigation of the Acoustical Properties of the Armory at the University of Illinois. F. R. WATSON.

New Electromagnetic Phenomena demonstrated by Floating Sand, Pebbles and other Non-conductors in Acidulated Water. (By title.) J. C. LINCOLN.

The Phonotrope, a New Instrument for finding the direction of an Acoustical Ray. A. G. WEBSTER.

The Propagation of Transverse Waves in a Bar. LOUIS THOMPSON.

The Exceptions to the Law of Dulong and Petit. (By title.) J. E. SIEBEL.

Experiments with Slow Positive Rays. A. G. DEMPSTER.

Theory of the Free Vibrations of a Lecher System. F. C. BLAKE.

Springs of Minimum Weight. (By title.) HENRY C. LORD.

Spectra of Some Halogen Compounds and Phenomena Connected Therewith. CHARLES SHEARD AND C. S. MORRIS.

On a New Method of using the Reversible Pendulum for the Determination of "g." J. C. SHEDD.

The Effect of Absorbed Gases in Photoelectric Emission. ROBERT J. PIERSOL. (Read by E. P. LEWIS.)

At the special session in charge of Section B on Wednesday afternoon the following program was presented:

The Dependence of Progress in Science upon the Development of Instruments. (Vice-Presidential Address before Section B) ANTHONY ZELENY.

A General Survey of the Field of High Pressure. P. W. BRIDGMAN. Discussion by A. G. Webster.

The Northrup Visible Molecules Apparatus was demonstrated at the close of the session by A. Zeleny.

At a short business session on Wednesday the result of the mail ballot for officers for 1916 was announced as follows: for president R. A. Millikan of Chicago; vice-president, H. A. Bumstead of New Haven; secretary, A. D. Cole of Columbus; treasurer, J. S. Ames of Baltimore; members of council, Irving Langmuir of Schenectady and G. B. Pegram of New York; members of editorial board, A. Trowbridge, E. P. Lewis and W. C. Sabine.

The amendments to the Constitution proposed at the Chicago meeting (designed to incorporate into the Constitution the more important features of the adoption of the PHYSICAL REVIEW as the organ of the Society) were adopted. On recommendation of the Council that an effort to secure an endowment for the support of the PHYSICAL REVIEW be made, the following motion was adopted: That the American Physical Society declares that the present advance of production in physical research in this country, as well as the actual conditions in Europe, render absolutely necessary the increase of means of publication; that to this end it is essential that an ample endowment be secured and that a committee be appointed by the President to inaugurate an effort to secure such endowment.

It was voted that a committee be appointed to consider how the Society can be made more useful to teachers in colleges and in secondary schools.

The report of the editor of the PHYSICAL REVIEW was presented and on motion accepted and placed on file. It showed an excess of receipts over expenditures for the year of $984.28.

The report of the treasurer of the Society was received after adjournment. It shows receipts for the year of $4,295.28 and disbursements $4,248.34. Excess receipts over expenditures for the year $46.94. In bank December 1, 1915, $676.69. Number of members 703. It is probable that both of these reports will be printed in full and sent by mail to all members.

The registration for the meeting was 158. The attendance at every session exceeded one hundred. About one hundred were present at the Physicists' dinner on Wednesday evening. Whether judged by the number and character of the papers presented, by the attendance or by the amount and interest of the discussion following the papers, this meeting was one of the best that the American Physical Society has ever held.

A. D. COLE,
Secretary.

ON A SUPPOSED ALLOTROPY OF COPPER.[1]

BY G. K. BURGESS AND I. N. KELLBERG.

MESSRS. E. COHEN and W. D. Helderman conclude from dilatometric observations that copper exists in two allotropic forms with a transition point at about 70° C. Several series of observations by three electrical re-

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 26–27, 1915.

sistance methods, sensitive to 1 part in 500,000 with copper wire of 0.05 mm. diameter, fail to give any indication of a discontinuity in the range 0 to 100° C. We therefore conclude the system copper is a stable one at ordinary temperatures and are able to find no evidences of allotropy.

NATIONAL BUREAU OF STANDARDS.

SENSITIVE PHOTOELECTRIC CELLS AND A PHOTOELECTRIC RELAY.[1]

BY JAKOB KUNZ AND J. STEBBINS.

A DESCRIPTION of very sensitive photoelectric cells, containing the alkali metals and helium, argon and neon is given. The cells are exhibited at the same time. They are used in stellar photometry. The high sensitiveness of these cells suggested that the construction of a photoelectric relay which may be used for various scientific and technical purposes. In one part of the apparatus the current is of photoelectric origin, in the other the current is due to ionization by collision, which may assume comparatively large values.

1. It is possible to determine the amount of work necessary to the production of ions in alkalivapors by collision.

2. The reversed photoelectric effect can be studied.

3. It can be used for photometric measurements.

4. For the detection of electromagnetic waves.

5. As a thermostat for the regulation of temperature within a very small fraction of a degree.

6. As a telephone relay for weak electric currents.

7. Lecture experiments have been performed by means of this relay, in which a beam of light is made to ring a bell or to light a series of incandescent lamps.

UNIVERSITY OF ILLINOIS.

THE DISTRIBUTION OF ELECTRONS IN A SUBSTANCE THAT CAN EXIST IN BOTH THE CONDUCTING AND THE NON-CONDUCTING STATES.[1]

BY L. E. DODD.

METALLIC selenium in the crystalline form is an electrical conductor. In the amorphous form it is a good insulator. When crystals of the substance are melted, there is, therefore, a change from the conducting to the non-conducting state. By observation as to whether any appreciable quantity of electricity is absorbed or released by selenium during the melting of the crystals, some knowledge can be gained as to the distribution per atom, in both states of the element, of those electrons that have to do with electric conduction in the crystals.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 26–27, 1915.

A simple experiment consisted in melting, by a focus of sun's rays, some selenium crystals that rested in a metallic cup attached to a delicate electroscope, previously charged. As the change from the conducting to the non-conducting state proceeded, no appreciable variation in the electroscope deflection was observed, save that which was experimentally accounted for by leak. The same results were observed regardless of the sign of charge on the electroscope. Crystals were also melted, in a similar manner, with the metallic cup connected to a quadrant electrometer. One pair of the quadrants was grounded and the other, connected with the cup, was initially at ground potential. No appreciable charging effect was observed under these circumstances. Obviously, the fact that the crystals were at a potential other than zero in the first case had no effect in preventing a transfer of charge. The same experiments, with electroscope and quadrant electrometer, were repeated, with a use of rays focused from an arc rather than the sun, with the same results.

Thus, there is clearly the experimental conclusion that no appreciable charge is either absorbed or liberated by the selenium during its change from the conducting to the non-conducting state. This means that the number of conducting electrons per atom in a crystal is the same as that of these same electrons, which have become non-conducting, in the amorphous, insulating mass of the melted crystal. The experiment favors the view that the conducting electrons in selenium crystals are not "free," like gas molecules, in which case one might expect their liberation from the substance when the crystal is melted, but are within reach of parent atoms, and thus belong to the atomic structures. One may imagine that, as the crystal melts, the conducting electrons so change their relations in the atomic structures as to become non-conducting.

STATE UNIVERSITY OF IOWA.

TALBOT'S BANDS AND THE RESOLVING POWER OF SPECTROSCOPES.[1]

BY THOMAS E. DOUBT.

A BRIEF sketch of the history of Talbot's bands is given with bibliography. Diagrams show arrangements for forming bands with prism, grating, and echelon spectroscopes. Photographs illustrate both high and low resolving power of spectroscopes.

Plane parallel glass plates from 3 mm. to 92 mm. in thickness were used to retard half the beam in the spectroscopes of high resolving power. Instruments from the Bunsen-Kirchoff type to Michelson's 8 in. gratings were tested.

The usual statement in introduction to Talbot's bands is that they are formed "when half the aperture of the pupil is covered with a thin plate of mica or glass," can be generalized and not limited if we have sufficient resolving power.

The fact that 1 mm. of glass produces one interference fringe for about six Ångström units in the region near the sodium lines suggests that we have here an objective standard of resolving power for spectroscopes. A discussion of

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 26–27, 1915.

the usual definition of resolving power and its connection with this objective standard follows. It is pointed out that if we are to understand the phenomena of light, we must coordinate the ether pulse theory of radiation with the undulatory theory of interference.

ARMOUR INSTITUTE OF TECHNOLOGY.

THE MEASUREMENT OF OPTICAL ROTATION IN THE INFRA-RED SPECTRUM.[1]

BY L. R. INGERSOLL.

BY a modification of the method already developed and used by the writer for measuring magnetic rotation of the plane of polarization of infra-red radiation it has been found possible to measure the rotation of sugar solutions and other naturally active liquids over a region of the spectrum extending from the D lines to about wave-length 2.2μ, with an accuracy about that of visual measurements.

Preliminary results for three sugar solutions and two organic liquids show a marked effect of an absorption band beyond 3μ on the rotation dispersion. It is planned to make a comparative study of the natural and magnetic rotation dispersion for a number of substances.

THE UNIVERSITY OF WISCONSIN.

THE CAUSE OF THE VARIATION OF THE EMANATION CONTENT OF SPRING WATER.[1]

BY R. R. RAMSEY.

LAST year at the Chicago meeting of the Physical Society I presented a paper in which I called attention to the fact that the emanation content of Indiana and Ohio springs varied from time to time. During nine months of the past year I have measured the radioactivity of two springs once every week. At the same time the flow of one of the springs was measured. These measurements show that the emanation content of the water increases and decreases as the flow increases and decreases. The flow of all springs in this locality varies with the rainfall. These facts and the fact that some of the highest values of the emanation content of spring water were obtained from "wet weather" springs a short time after very heavy rains, point to the conclusion that the rainwater in percolating through the soil dissolves and carries down with it some of the emanation which is continually moving upwards from the center of the earth to the surface. During dry weather when the flow is not rapid a large per cent. of the emanation which was dissolved in the water is transformed into radium A, B, C, and D, before the water issues from the ground. This conclusion is in accord with the observation of Wright and Smith[2] in which they show that the amount of emanation which issues from the soil is decreased as much as 50 per cent. at times after heavy rains.

INDIANA UNIVERSITY.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 26–27, 1915.

[2] PHYS. REV., Vol. 5, p. 459, 1915.

A THEORY OF THE INITIAL CONDITIONS OF THE CORONA.[1]

BY JAKOB KUNZ.

A DESCRIPTION of the numerous phenomena is given which are connected with the corona discharge. The difference between positive and negative electricity appears in electrical, optical, mechanical and probably chemical effects. The thickness of the luminous layer has been shown to be independent of the radius of the wire. A certain amount of energy will have to be accumulated before the luminous discharge appears; this assumption leads directly to the law that the critical electric force at the surface of the wire is inversely proportional to the square root of the radius of the wire. The constants in this relation are different for the positive and the negative corona. By means of the theory of ionization by collision the influence of the pressure can be accounted for.

UNIVERSITY OF ILLINOIS.

ON THE OPTICAL PROPERTIES OF AN ISOLATED CRYSTAL OF SELENIUM.[1]

BY CHARLES H. SKINNER.

A SELENIUM crystal, having a surface about 2 mm. by 5 mm. has been employed in a determination of its optical constants. The method of the Babinet's compensator was used. It was found that when the crystalline axis of the hexagonal crystal was held in a vertical position, the results obtained agreed well with the best published results for crystalline selenium in mass, but when the axis was held in a horizontal position, quite different results were obtained. This points to the possibility that all such crystalline substances that reflect metallically have in general three sets of principal optical constants (two in any one plane), and that when one determines the optical constants for a crystalline substance, used in mass, one really obtains only a certain mean set of values.

STATE UNIVERSITY OF IOWA.

ATOMIC MODELS IN WHOSE BEHAVIOR A MAGNETIC FIELD IS AN IMPORTANT FACTOR.[1]

BY ERNEST MERRITT.

WHEN an electron moves under the influence of a central force $F(r)$ in a magnetic field H normal to the plane of motion the chief effect of the magnetic field is to produce a uniform rotation of the axis of the orbit. This is perhaps most clearly indicated by the fact that the equation of motion may be put into the form

$$m(\ddot{r} - r\dot{\varphi}^2) = F(r) - mr\omega,^2$$

$$mr^2\dot{\varphi} = \text{const.},$$

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 26–27, 1915.

where φ is the angle between the radius vector to the electron and a reference axis through the center which rotates with the constant angular velocity

$$\omega = \frac{He}{2m}.$$

If there is no magnetic field the equations of motion are

$$m(\ddot{r} - r\dot{\theta}^2) = f(r) \quad mr^2\dot{\theta} = \text{constant}.$$

where θ measures the angular displacement of the radius vector from a fixed axis. If

$$f(r) = F(r) - mr\omega^2$$

the equations are of the same form. It appears therefore that the effect of a magnetic field is to produce the same motion relative to the rotating axis as would be produced, without a magnetic field and without rotation of the axis of reference, by a central force

$$F(r) - mr\omega^2.$$

An interesting special case is that in which the force $F(r)$ is a repulsion. With suitable starting conditions the motion with reference to the rotating axis will consist of a vibration about the point for which $F(r) = mr\omega^2$. The vibrations will be simple harmonic for infinitely small amplitudes, but in general "overtones" will be present. In such cases

$$r = r_0 + A \cos(pt + \varphi_1) + B \cos(2pt + \varphi_2) + \cdots$$

and the displacement of the electron in the direction of some *fixed* axis OX is

$$x = r \cos \omega t = r_0 \cos \omega t + A \cos \omega t \cos(pt + \varphi_1) + B \cos \omega t \cos(2pt + \varphi_2) + \cdots.$$

Each term of the form $\cos \omega t \cos(npt + \varphi_n)$ can be broken up into the sum of two terms of the form

$$\cos\{(\omega + np)t + \psi\} \text{ and } \cos\{(\omega - np)t + \psi\}.$$

The radiation from an electron moving in this manner would therefore contain lines having frequencies proportional to $\omega, \omega + p, \omega - p, \omega + 2p, \omega - 2p$, etc. In other words, the spectrum would consist of a series of lines equally spaced on the frequency scale. Since the amplitude will ordinarily be less for the higher harmonics we should expect the central line, of frequency ω, to be brightest, while the brightness will fall off progressively on both sides of the central line. Such a spectrum would have the general characteristics of the fluorescence spectrum of the uranyl salts, although the numerical relations would be different.

While this simple case can scarcely be expected to correspond to any actual atomic structure it serves to illustrate a general principle. The same method of analysis can, for example, be employed in any case where the orbit described under the action of the force $F(r) - mr\omega^2$ is a closed curve. In many cases where the orbit is not closed it may be regarded as at least approximately equivalent to a closed orbit whose principal axes are rotating, and these cases also may be treated in much the same way. It should be noted also that the same general method may be employed in cases where the force on the electron is in part due to the action of other moving electrons. It will be recalled that the question of stability introduces difficulties in the case of the Saturnian type of atomic model, especially in the Nagaoka or Rutherford form in which the positive charge is concentrated. These difficulties are made less by the assumption of a magnetic field.

The existence of a strong magnetic field in the neighborhood of each molecule of a crystal like uranium nitrate seems highly probable, for the molecules would not be in stable equilibrium under the action of electrical forces alone. That the magnetic field should be uniform over the whole orbit of an electron is scarcely to be expected, however, since it is reasonable to expect that the field due to the molecule itself, which probably varies rapidly with the distance, will be an important part of the whole. If the fluorescence spectrum of the uranium salts is really produced in some such manner as that here suggested we must therefore assume special conditions, which are made possible perhaps by the molecular structure of the uranyl radical. The magnetic field required is of the same order of magnitude as the internal field predicted by the electron theories of magnetism.

CORNELL UNIVERSITY.

THE REFLECTION OF SOUND.[1]

BY F. R. WATSON.

THIS work is a continuation of the investigation on the transmission of sound.[2] Sound from a steadily blown whistle mounted at the focus of a parabolic mirror is directed toward an open doorway. This is assumed to give zero reflection. Layers of material are then placed over the doorway and the intensity of reflected sound measured by a Rayleigh resonator. The data obtained furnishes an explanation for the anomalous transmitting action of some materials.

UNIVERSITY OF ILLINOIS.

[1] Abstract of paper presented at the Chicago meeting of the Physical Society, November 26, 27.

[2] PHYSICAL REVIEW, April, 1915.

THE EXCEPTIONS TO THE LAW OF DULONG AND PETIT.[1]

BY J. E. SIEBEL.

IN order to mitigate the apparent exceptions to the law of Dulong and Petit, the author undertakes to show a simple way to calculate the specific heat at low temperatures in accordance with the kinetic heat theory. For this purpose, instead of comparing specific heats, the total heat energy which a body should contain according to the kinetic heat theory, is compared with the energy which it contains in accordance with the molecular heat observed by Nernst and others at given temperatures. The resulting difference of energy is found to be almost a constant function of the different temperatures under observation, characteristic for every individual substance. According to the author, this is due to a nearly constant amount of potential molecular energy, probably chiefly of gravitation and expressible by formulæ in harmony with observed data, characterizing them as functions of the specific heat derived from the Dulong and Petit proposition in accordance with the kinetic heat theory.

CHICAGO, ILL.

[1] Abstract of a paper presented at the Columbus meeting of the Physical Society, December 28–30, 1915.